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**SEPARATION SYSTEM OF METAL POWDER FROM SLURRY AND PROCESS**

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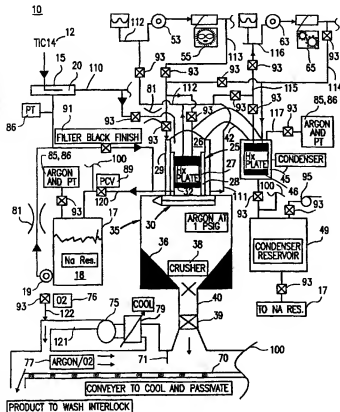
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[Continued on next page]

(54) Title: SEPARATION SYSTEM OF METAL POWDER FROM SLURRY AND PROCESS



(57) Abstract: A system and method of separating metal powder from a slurry of liquid metal and metal powder and salt is disclosed in which the slurry is introduced into a first vessel operated in an inert environment when liquid metal is separated from the metal powder and salt leaving principally salt and metal powder substantially free of liquid metal. The salt and metal powder is transferred to a second vessel operated in an inert environment with both environments being protected from contamination. Then the salt and metal powder are treated to produce passivated powder substantially free of salt and liquid metal. The method is particularly applicable for use in the production of Ti and its alloys.



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## **SEPARATION SYSTEM OF METAL POWDER FROM SLURRY AND PROCESS.**

### **Background of the Invention**

This invention relates to a separation system and process as illustrated in Fig. 1 useful for the product produced by Armstrong method as disclosed and claimed in U.S. Patents 5,779,761; 5,958,106 and 6,409,797, the disclosures of each and every one of the above-captioned patents are incorporated by reference.

### **Summary of the Invention**

A principal object of the invention is to provide a separation system for the Armstrong process disclosed in the '761, '106 and '797 patents;

Another object of the invention is to provide a continuous separation system.

The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

### **Brief Description of the Drawings**

Figure 1 is a schematic illustration of the separation system of the present invention.

### **Detailed Description of the Invention**

The system 10 of the present invention deals with the separation of a metal, alloy or ceramic product, such as titanium, for example only, from the reaction products in the Armstrong process. Although the Armstrong process is applicable to a wide variety of exothermic reactions, it is principally applicable to metals, mixtures, alloys and ceramics disclosed in the above-mentioned patents. The product of Armstrong process is a slurry of excess reductant metal, product metal and alloy or ceramic and salt produced from the reaction. This slurry has to be separated so that various parts of it can be recycled and the produced metal, alloy or ceramic separated and passivated if necessary.

Turning now to the schematic illustration of the system and process of the present invention illustrated in Fig. 1, there is disclosed in the system 10 a source of, for illustration purposes only, titanium tetrachloride 12 which is introduced into a reactor

15 of the type hereinbefore disclosed in the Armstrong process. A supply tank or reservoir 17 with a supply of sodium (or other reductant) 18 is transferred by a pump 19 to the reactor 15 wherein a slurry product 20 of excess reductant and metal, alloy or ceramic, and salt is produced at an elevated temperature, all as previously described in the incorporated patents.

The slurry product 20 is transferred to a vessel 25 which is in the illustration dome-shaped, but not necessarily of that configuration, the vessel 25 having an interior 26 into which the slurry product 20 is introduced. A filter 27, preferably but not necessarily cylindrical, is positioned within the interior 26 and defines an annulus 28, the slurry product 20 being received inside the cylindrical filter 27. An annular heat exchanger 29 is positioned around the vessel 25, all for a purpose hereinafter disclosed.

The vessel 25 further includes a moveable bottom closure 30. Heat exchange plates 32 are connected as will hereinafter be described to an isolated heating system 50. A collection vessel 35 is positioned below the vessel 25 and is sealed therefrom by the moveable bottom closure 30. The collection vessel 35 has an inwardly sloping bottom surface 36 which leads to a crusher 38 and a valve 39 in the outlet 40 of the collection vessel 35.

Finally, a vapor conduit 42 interconnects the top of the vessel 25 and particularly the interior 26 thereof with a condenser vessel 45, the condenser vessel having a heat exchange plate 46 connected, as hereinafter described, to an isolated cooling system 60. The condenser 45 is connected to a condenser reservoir 49, the condensate collected therein being routed to the sodium supply tank or reservoir 17.

The isolated heating system 50 includes a head tank 52 for the heating fluid which is moved by pump 53 to the heater 55 as will be hereinafter described, connected to both the heat exchanger 29 surrounding the vessel 25 and the heat exchange plates 32 interior of the vessel 25. The isolating cooling system 60 also is provided with a head tank 62, a pump 63 and a cooler 65 which serves to cool the cooling fluid circulated in an isolated loop to the cooling plates 46 as will be hereinafter set forth.

Below the valve 39 and the collection vessel 35 is a product conveyor 70 having a baffle or cake spreader 71 extending downwardly toward the conveyor 70. The

conveyor 70 onto which the produced metal, alloy or ceramic and salt are introduced from the collection vessel 35, after removal of the excess reductant metal, is contacted with a counter current flow of gas, preferably but not necessarily oxygen and argon, 77 from a blower 75 in communication with a supply 76 of oxygen and the supply of inert gas such as argon. The heat exchanger 79 is in communication with the blower 75 so as to cool the oxygen/argon mixture 77 as it flows in counter current relationship with the produced metal, alloy or ceramic on the conveyor 70, thereby to contact the product particulates with oxygen to inert the produced metal, alloy or ceramic when required but not so much as to contaminate the produced material.

As indicated in the flow sheet of Fig. 1, there are a plurality of flow meters 81 distributed throughout the system, as required and as well known in the engineering art. There are pressure transducers 86 and pressure control valves 89 where required, all within the engineering skill of the art. A back filter valve 91 is provided in order to flush the filter 27 if necessary. Additionally, a variety of standard shut-off valves 93 are positioned within the loop, hereinafter to be explained and as required. A vacuum pump 95 is used to draw a vacuum in the vessel 25, as will be explained, and the symbol indicated by reference numeral 100 indicates that a plurality of the same or similar systems may be operating at any one time, it being remembered that the enclosed figure is for a single reactor 15 and one separation vessel 25, wherein as in a commercial production plant, a plurality of reactors 15 may be operating simultaneously each reactor 15 may have more than one separation vessel 25, all depending on engineering economics and ordinary scale up issues.

Product 20 from the reactor 15 exits through line 110 and enters vessel 25 at the top thereof. Although line 110 is shown entering above the filter 27, preferably the line 110 and filter 27 are positioned so that slurry 20 is introduced below the top of filter 27 or in the center of the filter or both. As described in the previously incorporated patents, the slurry product 20 consists of excess reductant metal, salt formed by the reaction and the product of the reaction which in this specific example is titanium existing as solid particles. The product 20 in slurry form from the reactor 15 is at an elevated temperature depending on the amount of excess reductant metal present, the heat capacity thereof and other factors in the reactor 15 during operation of the Armstrong

process. In the vessel 25 is a filter 27 which occupies a portion of the interior 26 of the vessel 25, the interior optionally being heated with the annular heat exchanger 29. The slurry product 20 is directed to the interior of the filter 27 where the slurry contacts the heat exchange plates 32.

In the heating system 50, the heat exchange fluid in the plates 32 pass with the heat exchange fluid from the annular heat exchanger 29 through line 111 to the line 112 which connects the heat exchange medium supply in the head tank 52 to the heat exchanger 55. Fluid moves from the heater 55 through the heat exchange plates 32 by means of the pump 53 as the heated heat exchange fluid flows out of the heat exchanger 55 through line 113 and back into the heat exchange plates 32 and/or the annular heat exchanger 29. Because the heating system 50 is a closed loop, the heat exchange fluid may or may not be the same as the reductant metal used in the reactor 15. NaK is shown as an example because of the low melting point thereof, but any other suitable heat exchange fluid may be used. Suitable valves 93 control the flow of heat exchange fluid from the heater 55 to either or both of the heat exchanger 29 and plates 32. Preferably, the plates 32 are relatively close together, on the order of a few inches, to provide more heat to the cake which forms as excess reductant metal vaporizes. Moreover, closer plates 32 reduce the path length the heat has to travel and the path length the excess reductant metal vapor travels through the forming cake, thereby to reduce the time required to distill and remove excess reductant metal from the vessel 25. Exact spacing of the plates 32 depends on a number of factors, including but not limited to, the total surface area of the plates, the heat transfer coefficient of the plates, the amount of reductant metal to be vaporized and the temperature differential between the inside and the outside of the plates.

When the slurry product 20 comes out of the reactor 15, it is at a pressure at which the reactor 15 is operated, usually up to about two atmospheres. The product slurry 20 enters the inside of filter 27 under elevated pressure and gravity results in the liquid reductant metal being expressed through the filter 27 into the annular space 28 and fed by the line 120 into the reservoir 17. The driving force for this portion of the separation is gravity and the pressure differential between the reactor 15 and the inlet pressure of pump 19. If required the annulus 28 may be operated under vacuum to

assist removal of liquid reductant metal, or the pressure in vessel 25 may be increased during the deliquoring of the reductant metal. After sufficient liquid metal has drained through the filter 27 by the aforementioned process, the PCV valve 89 is closed and other valves 93 are closed to isolate vessel 25 and then the valve 93 to the vacuum pump 95 is opened, whereupon a vacuum is established in the interior 26 of vessel 25. Heating fluid (liquid or vapor, for instance Na vapor) is directed into the heat exchanger plates 32 to boil the remaining reductant metal 18 producing a filter cake. The temperature in vessel 25 is elevated sufficiently to vaporize remaining liquid metal reductant 18 therein which is drawn off through conduit 42 to the condenser 45. The conduit 42 is required to be relatively large in diameter to permit rapid evacuation of the interior 26 of the vessel 25. Because the pressure drop between the vessel 25 and the condenser 45, during vaporization of the reductant metal 18 is low, the specific volume is high and the mass transfer low, requiring a large diameter conduit 42. Boiling the reductant metal on the shell side is accomplished by heat exchange with a heated fluid on the tube side.

The annular heat exchanger 29 is optionally operated to maintain the expressed liquid in the annulus 28 at a sufficient temperature to flow easily and/or to provide additional heat to the vessel 25 to assist in vaporization of excess reductant metal from the interior 26 thereof. After liquid metal reductant vapor has been removed from the interior 26 of the vessel 25, a filter cake remains from the slurry 20. The appropriate valves 93 are closed and the vacuum pump 95 is isolated from the system.

In the condenser 45, heat exchange plates 46 are positioned in order to cool the reductant metal vapor introduced therein. The cooling system 60 is operated in a closed loop and maintained at a temperature sufficiently low that reductant metal vapor introduced into the condenser 45 condenses and flows out of the condenser, as will be disclosed. The cooling system 60 includes a cooler 65 as previously described and the pump 62. The coolant exits from the cooler 65 through line 114 which enters the heat exchange plates 46 and leaves through a line 115 which joins the line 116 to interconnect the head tank 62 and the cooler 65. As seen in the schematic of Fig. 1, the heat exchange fluid used in the heating system 50 and the cooling system 60 may



be the same or may be different, as the systems 50 and 60 can be maintained separately or intermixed.

Both the vessel 25 and the condenser 45 are operated at least part of the time under a protective atmosphere of argon or other suitable inert gas from the argon supply 85, the pressure of which is monitored by the transducer 86, the (argon) supply inert gas 85 being connected to the condenser 45 by a line 117, the condenser 45 also being in communication with the vessel 25 by means of the oversized conduit 42. Further, as may be seen, each of the heating system 50 and the cooling system 60 is provided with its own pump, respectively 53 and 63. As suggested in the schematic of Fig. 1, the heating and cooling fluid may, preferably be NaK due to its lower melting point, but not necessarily, and as an alternative could be the same as the reductant metal in either liquid or vapor phase, as disclosed.

After sufficient reductant metal 18 has been removed from the slurry 20, via the filter 27 and the conduit 42, remaining therein is a combination of the titanium product in powder form and salt made during the exothermic reaction in reactor 15. Because the resultant dried cake has a smaller volume than the slurry product 20 introduced, when the movable bottom closure 30 is opened, the dry cake falls from the filter 27 into the collection vessel 35 whereupon the combination of salt and titanium fall into the crusher 38 due to the sloped bottom walls 36. In the event the cake does not readily fall of its own accord, various standard vibration inducing mechanism or a cake breaking mechanism may be used to assist transfer of the cake to the collection vessel 35. The collection vessel 35 as indicated is maintained under an inert atmosphere at about atmospheric pressure, and after the cake passes through the crusher 38 into the exit or outlet 40, the cake passes downwardly through valve 39 onto the conveyor 70. There is a cake spreader or baffle 71 downstream of the valve 39 which spreads the cake so that as it is contacted by a mixture 77 of inert gas, preferably argon, and oxygen flowing counter-current to the direction of the product, the titanium powder is passivated and cooled. Although the conveyor 70 is positioned in Fig. 1 horizontally, it may be advantageous to have the conveyor move upwardly at a slant as a safety measure in the event that closure 30 fails, then excess reductant metal would not flow

toward a water wash. In addition, there may be cost advantages in having the product wash equipment on the same level as the separation equipment.

Cooling and passivating is accomplished in the cooler 79 with blower 75 which blows a cooled argon and oxygen mixture through a conduit 121 to the product, it being seen from the schematic that the counter-current flow of argon and oxygen with the product has the highest concentration of oxygen encountering already passivated and cooled titanium so as to minimize the amount of oxygen used in the passivation process. Oxygen is conducted to the system from a supply thereof 76 through a valve 93 and line 122 and is generally maintained at a concentration of about 0.1 to about 3% by weight. The mixture of passivated titanium and salt is thereafter fed to a wash system not shown. Various flow meters 81 are positioned throughout the system as required, as are pressure control valves 89 and pressure transducers 86. A filter backwash valve 91 is positioned so that the filter 27 can be backwashed when required if it becomes clogged or otherwise requires backwashing. Standard engineering items such as valves 93, vacuum pump 95 and pressure transducers 86 are situated as required. Symbol 100 is used to denote that parallel systems identical or similar to all or a portion of the system 10 illustrated may be operated simultaneously or in sequence.

In the Armstrong process, the production of the metal, alloy or ceramic is continuous as long as the reactants are fed to the reactor. The present invention provides a separation system, apparatus and method which permits the separation to be either continuous or in sequential batches so rapidly switched by appropriate valving as to be as continuous as required. The object of the invention is to provide a separation apparatus, system and method which allows the reactor(s) 15 in a commercial plant to operate continuously or in economic batches. Reduction of the distillation time in vessel 25 is important in order to operate a plant economically, and economics dictate the exact size, number and configuration of separation systems and production systems employed. Although described with respect to Ti powder, the invention applies to the separation of any metal, alloy thereof or ceramic produced by the Armstrong process or other industrial processes.

The heating mechanism shown is by fluid heat exchange, but heaters could also be electric or other equivalent means, all of which are incorporated herein. The bottom closure 30 is shown as hinged and is available commercially. The closure 30 may be clamped when shut and hydraulically moved to the open position; however, sliding closures such as gate valves are available and incorporated herein. Although the reactor 20 is shown separate from the vessel 25, the invention includes engineering changes within the skill of the art, such as but not limited to incorporating reactor 20 into vessel 25. Although vessel 35 is illustrated in one embodiment, the vessel 35 could easily be designed as a pipe. Also, the crusher 38 could be located in vessel 25 or intermediate vessel 25 and vessel 35. Moreover, the cake forming on the filter 27 may be broken up prior to or during or subsequent to removal of the liquid metal therefrom. Similarly, when referring to an inert environment, the invention includes a vacuum as well as an inert gas. An important feature of the invention is the separation of vessels 25 and 35 so the environments of each remain separate. That way, no oxygen can contaminate either vessel.

In one specific example, a reactor 15 producing 2 million pounds per year of titanium powder or alloy powder requires two vessels 25, each roughly 14' high and 7' in diameter with appropriate valving, so that the reactor 15 would operate continuously and when one vessel 25 was filled, the slurry product from the reactor would switch automatically to the second vessel 25. The fill time for each vessel 25 is the same or somewhat longer than the deliquor, distill and evacuation time for vessel 25.

Changing production rates of reactor 15 simply requires engineering calculations for the size and number of vessels 25 and the related equipment and separation systems. The invention as disclosed permits continuous production and separation of metal or ceramic powder, while the specific example disclosed permits continuous separation with two or at most three vessels 25 available for each reactor 15. With multiple reactors 15, the number of vessels 25 and related equipment would probably be between 2 and 3 times the number of reactors.

While there has been disclosed what is considered to be the preferred embodiment of the present invention, it is understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

**WHAT IS CLAIMED IS:**

1. A method of separating metal powder from a slurry of liquid metal and metal powder and salt, comprising introducing the slurry into a first vessel operated in an inert and/or vacuum environment for separation of liquid metal from the metal powder and salt leaving principally salt and metal powder substantially free of liquid metal, transferring the salt and metal powder substantially free of liquid metal to a second vessel operated in an inert environment, and thereafter treating the salt and metal powder to produce passivated metal powder substantially free of salt and liquid metal.
2. The method of claim 1, wherein the inert environment is an argon atmosphere.
3. The method of claim 1, wherein the salt and metal powder are crushed to form clumps having diameters less than about five centimeters prior to passivation.
4. The method of claim 1, wherein the liquid metal is separated from the salt and metal powder in the first vessel both as a liquid and as a vapor.
5. The method of claim 4, wherein the liquid metal vapor from the first vessel is transferred to a condenser operated in an inert environment.
6. The method of claim 4, wherein the liquid metal is an alkali or an alkaline earth metal or mixtures thereof.
7. The method of claim 6, wherein the salt is a halide.
8. The method of claim 7, wherein the metal powder is titanium or a titanium alloy.
9. The method of claim 8, wherein the titanium or titanium alloy is CP 1 to CP 4.
10. The method of claim 9, wherein the metal powder has diameters in the range of from about 0.1 to about 10 microns.
11. The method of claim 1, wherein passivation occurs on a conveyor.
12. The method of claim 11, wherein the metal powder is continuously cooled and passivated.

13. The method of claim 1, wherein the environments of the first and second vessels are protected from contamination by oxygen during the production of metal powder substantially free of salt and liquid metal.

14. A method of separating metal powder from a slurry of liquid metal and metal powder and salt formed by introducing a metal halide vapor subsurface of a liquid metal causing an exothermic reaction producing salt and metal powder with the liquid metal being present in excess of the stoichiometric amount required, comprising introducing the slurry into a first vessel operated in an inert and/or vacuum environment for filtration and vaporization of liquid metal from the metal powder and salt leaving principally salt and metal powder substantially free of liquid metal, transferring the liquid metal vapor to a condenser operated in an inert environment to convert the liquid metal vapor to a liquid to be recycled for production of additional metal powder, transferring the salt and metal powder substantially free of liquid metal to a second vessel operated in an inert environment, and thereafter treating the salt and metal powder to produce passivated metal powder substantially free of salt and liquid metal.

15. The method of claim 14, wherein the slurry is heated in the first vessel by contact with a heat exchanger internal to the first vessel having heat exchange fluid pumped therethrough.

16. The method of claim 14, wherein the liquid metal vapor from the first vessel is cooled by contact with heat exchanger internal to the condenser having a heat exchange fluid pumped therethrough.

17. The method of claim 14, wherein the first vessel is heated by both an internal and an external heat exchanger.

18. The method of claim 14, wherein the slurry is introduced into the interior of a candle filter in the first vessel with liquid metal flowing through the candle filter and out of the first vessel.

19. The method of claim 14, wherein the inert environment for the first and second vessels is an argon atmosphere.

20. The method of claim 19, wherein the condenser is operated in an argon atmosphere.

21. The method of claim 14, wherein the environments of the first and second vessels are protected from contamination by oxygen during the production of metal powder substantially free of salt and liquid metal.

22. A system for separating metal powder from a slurry of liquid metal and metal powder and salt formed by introducing a metal halide vapor subsurface of a liquid metal causing an exothermic reaction producing salt and metal powder with the liquid metal being present in excess of the stoichiometric amount required, comprising a first inerted vessel in communication with a heater and a filter for filtering liquid metal from the slurry and for heating liquid metal to vaporize the liquid metal from the salt and metal powder forming a filter cake of salt and metal powder, an inerted condenser in communication with said first vessel for receiving metal vapor and converting same to liquid metal, a second inerted vessel in valved communication with said first inerted vessel for receiving filter cake therefrom; a crusher in or in communication with said second inerted vessel for crushing the filter cake; a cooling and passivating station for receiving crushed filter cake, and a valve mechanism intermediate said first and second vessel and between said second vessel and said cooling and passivating station to prevent air from contaminating said first and second vessels during transfer of filter cake from said first vessel to said cooling and passivating station.

23. The system of claim 22, wherein said heater in communication with said first inerted vessel is interior of said vessel.

24. The system of claim 23, wherein said heater interior of said inerted first vessel is in communication with a source of heat exchange fluid which optionally is dedicated to said heater.

25. The system of claim 22, wherein said filter in communication with said first inerted vessel is interior of said vessel.

26. The system of claim 25, wherein said filter is a filter forming an annulus with said first inerted vessel into which liquid metal flows, and further including a conduit

in communication with said annulus for transferring liquid metal from said first inerted vessel to an inerted liquid metal reservoir.

27. The system of claim 22, wherein said first and second inerted vessels are inerted with argon.

28. The system of claim 27, wherein said condenser is inerted with argon.

29. The system of claim 28, wherein said inerted condenser is in communication with an argon inerted reservoir for liquid metal formed from condensed metal vapor.

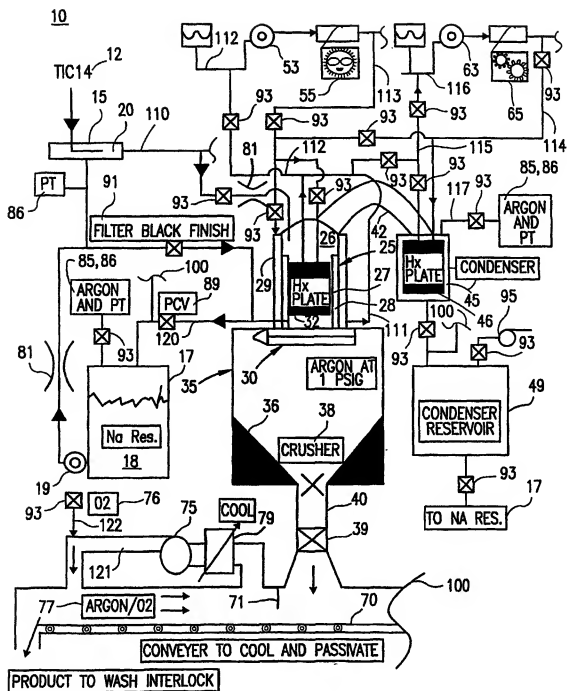
30. The system of claim 22, wherein said condenser is in communication with a source of heat exchange fluid which optionally is dedicated to said condenser.

31. The system of claim 22, wherein said valve intermediate said first and second inerted vessel is hinged to open into said second inerted vessel.

32. The system of claim 22, wherein said first and second vessel are integral.



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## INTERNATIONAL SEARCH REPORT

International application No  
PCT/US 03/27649A. CLASSIFICATION OF SUBJECT MATTER  
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According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum: documentation searched (classification system followed by classification symbols)

IPC 7 C22B 801D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, COMPENDEX

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	column 4, lines 24-29 and lines 49-55; column 7, lines 32-45	
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☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

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Information on patent family members

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REDUCTION OF METALS WITH LIQUID METAL REDUCING AGENTS

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(56) Prior Art Documents

26334/57 219663 15.6, 16.2

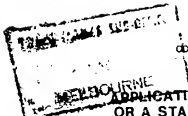
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(57) Claim

1. A method of obtaining a desired metal selected from the group consisting of metals capable of existing in the form of a compound capable of being reduced with a liquid metal reducing agent which comprises a reaction comprising contacting such a compound of said desired metal in substantially compact form with a liquid metal reducing agent being sodium and potassium metals at a temperature not greater than the boiling point or the sublimation point of the compound at the pressure of the reaction whereby to obtain said desired metal.
2. A method as claimed in claim 1, wherein said compound is a covalent halide.
4. A method of obtaining a desired metal selected from the group consisting of titanium, aluminium, iron, manganese, hafnium, zirconium, tantalum, vanadium, uranium and tungsten which comprises a reaction comprising contacting a halide of said desired

metal in substantially compact form with a liquid metal reducing agent being sodium and potassium metals at a temperature not greater than the boiling point or the sublimation point of the compound at the pressure of the reaction whereby to obtain said desired metal.

6. A method as claimed in claim 4, wherein said desired metal is aluminium.
15. A method as claimed in claim 13, wherein said liquid metal reducing agent addition alloy includes at least one of calcium and magnesium.



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APPLICATION FOR A STANDARD PATENT  
OR A STANDARD PATENT OF ADDITION

SECTION 34(4)(a) DIRECTION SEE FOLIO  
NAME DIRECTED

hereby apply for the grant of a ~~standard patent~~ for an invention entitled

*Reducing of Metals with liquid Metal Refining Agent*

which is described in the accompanying ~~provisional~~ ~~complete~~ specification

(To be included in the case of a Convention application)

Details of basic application(s) -

Number of basic application

Name of Convention country in which basic application was filed

Date of basic application

(To be included in the case of an application made by virtue of section 51)

Number of original application

Person by whom made

(To be included in the case of an application for a patent of addition)

I request that the patent may be granted as a patent of addition to the patent applied for on Application

No. Patent No.

In the name of

I request that the term of the patent of addition be the same as that for the main invention or so much of

the patent for the main invention as is unexpired

ADDRESS FOR SERVICE  
ALTERED

My address for service is

*Department of Mechanical Engineering*  
*University of Melbourne, Parkville 3052*

Dated this 25th day of May 19 84

To:

*W. D. R. Marks*

(Signature)

THE COMMISSIONER OF PATENTS

COMPLETE AFTER PROVISIONAL SPECIFICATION No 43017/55

This form must be accompanied by either a provisional specification (Form 9 and true copy) or by a complete specification (Form 10 and true copy).

\* These sections are to be completed only where applicable.

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DECLARATION IN SUPPORT OF AN APPLICATION FOR A PATENT

In support of the Application made by William R B Bulmer

for a patent for an invention entitled CHEMICAL PROCESSES

I, WILLIAM REGINALD BULMER MARTIN  
of 48 CUTHBERT STREET, CORINELLA, VIC 3984

do solemnly and sincerely declare as follows:—

1. I am the applicant for the patent.

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1. ~~I am not the applicant for the patent.~~

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2. ~~I am not the applicant for the patent.~~

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2.

of

~~I am not the applicant for the patent.~~

Declared at Melbourne this 25 day of May 1984

TO:

THE COMMISSIONER OF PATENTS.

W R B Bulmer

(Signature of Declarant)

(IMPORTANT Cross out inapplicable words in the above Form.)



587734 Form 10

PATENTS ACT 1952

## COMPLETE SPECIFICATION

(ORIGINAL)

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A. TATHOCK & ASSOCIATES (P.O. Box 358),  
21 QUEENSLAND ST, CARLTON SOUTH VIC 3052Complete Specification for the invention entitled: ~~CHEMICAL PROCESS~~  
Reducing of Metals with Liquid Metal Reducing Agents

The following statement is a full description of this invention, including the best method of performing it known

to the public.

Note: The description is to be typed in double spacing, pica type face, in an area not exceeding 250 mm in depth and 160 mm in width, on tough white paper of good quality and it is to be inserted inside this form.

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This invention relates to chemical processes. In another aspect this invention relates to chemical processes involving reactive metals(s) in the liquid state at temperatures and pressures such that the other reactants, generally covalent halides, are present in compact phase i.e. not in the <sup>gaseous</sup> gaseous phase.

I have found that in chemical process wherein one of the reactants is a suitable metal or is a suitable metal mixture, in the liquid state, substantial and unexpected advantages accrue from employment of the liquid metal in considerable stoichiometric excess. Inter alia, the invention takes advantage of the extraordinarily high capability to transfer heat which is exhibited by metals in the liquid state. The excess liquid metal also functions as a materials transfer agent.

The present invention provides a method of obtaining a desired metal selected from the group consisting of metals capable of existing in the form of a compound capable of being reduced with a liquid metal reducing agent which comprises a reaction comprising contacting such a compound of said desired metal in substantially compact form with a liquid metal reducing agent being sodium and potassium metals at a temperature not greater than the boiling point or the sublimation point of the compound at the pressure of the reaction whereby to obtain said desired metal.

Preferably said compound is a covalent halide.

Preferably said desired metal is selected from the group consisting of titanium, aluminium, iron, manganese, hafnium, zirconium, tantalum, vanadium, uranium and tungsten.



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In a particularly preferred aspect the present invention provides a method of obtaining a desired metal selected from the group consisting of titanium aluminium iron manganese hafnium zirconium tantalum vanadium uranium and tungsten which comprises a reaction comprising contacting a halide of said desired metal in substantially compact form with a liquid metal reducing agent being sodium and potassium metals at a temperature not greater than the boiling point or the sublimation point of the compound at the pressure of the reaction whereby to obtain said desired metal.

Particular advantage is derived from application of the



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1 invention to recovery of titanium from its tetrachloride  
2 which is directly derivable from ores such as rutile.

3 High purity titanium metal is today a strategic  
4 material, for example in space research and for high speed  
5 aircraft. It is expensive to produce by conventional means;  
6 firstly because it is so reactive at high temperatures,  
7 especially temperatures greater than 500°C and, it is  
8 particularly reactive with respect to oxygen.

9 A development of the invention envisages the  
10 preparation of alloys which are required to be free <sup>of</sup> ~~to~~  
11 impurities, particularly oxygen, such as iron titanium and  
12 titanium iron manganese alloys. Alloys such as these can be  
13 used to store hydrogen in the form of hydrides and the  
14 amount of hydrogen which can be stored is inversely  
15 dependant on the amount of oxygen contamination.

16 The alloys referred to above as hydrogen stores may  
17 provide a satisfactory source of hydrogen for use as a fuel  
18 for internal combustion engines and for storage of energy  
19 via the fully reversible heat of reaction.

20 Oxygen is ubiquitously present in air and water and  
21 only a few parts per million are required to adversely  
22 affect the properties of high purity titanium metal and the  
23 types of alloys mentioned herein. Consequently very special  
24 techniques are needed to produce titanium metal in oxygen-  
25 free condition.

26 It is recognized that "commercial pure" titanium  
27 capitalises upon the presence of impurity oxygen which is  
28 controlled, like carbon in steel, to increase the stiffness  
29 in ambient temperature conditions for corrosion resistant  
30 duty as in chemical plants.

31 Because of the special nature of the covalent titanium  
32 halide compounds, particularly the chlorides, it is possible  
33 to purify them entirely from oxygen reasonably easily and in  
34 a continuous plant. However, existing processes for recovery  
35 of titanium metal from the halide invariably result in  
36 surface contamination from air and/or water arising from  
37 recovery of the "sponge" from solidified melts. Only  
38 coarsely crystalline material with low surface/volume ratio



1 can be used for high purity metal. Fine titanium adsorbs so  
2 much water and/or air on its surface that subsequent melting  
3 under argon at minimum pressure to maintain an electric arc  
4 yields a metal ingot unacceptably high in oxygen for high  
5 purity metal. Furthermore, fine titanium powder is generally  
6 pyrophoric and must be handled in an inert atmosphere.

7 The invention is also applicable to the obtaining of  
8 other metals as noted above and of these another  
9 particularly economically significant metal is aluminium.  
10 However, care needs to be applied in obtaining an anhydrous  
11 halide and it is desirable that the halide be in liquid  
12 phase.

13 Many halides may be put in liquid phase, if that is not  
14 their normal condition, by heat and/or pressure so as to  
15 liquefy them but it is also possible to dissolve halides in  
16 inert solvents such as a paraffin or suspend it in a liquid  
17 or even use reactive solvents such as ferri chloride and  
18 titanium tetrachloride.

19 However, experimental work does show that even if the  
20 halide is in solid form reaction does occur.

21 Preferably said liquid metal reducing agent comprises a  
22 ~~metal selected from the group consisting of Group I metals~~  
23 ~~or a mixture of metals~~ containing a Group I metal.

24 Preferably said liquid metal reducing agent is a  
25 mixture of sodium and potassium alloy.

26 Said liquid metal reducing agent may contain at least  
27 one of calcium and magnesium.

28 It is desirable that said reaction is conducted at a  
29 temperature not greater than the boiling point or  
30 sublimation point of the halide under the pressure  
31 pertaining.

32 It is desirable that said reaction is conducted at a  
33 temperature such that solid by-product halides of said  
34 liquid metal reducing agent are formed.

35 The reaction is greatly exothermic. When using NaK  
36 alloy in the presence of approximately equivalent amounts of  
37 reactants without cooling, the evolved heat caused the  
38 reaction to "run away" with a resultant explosion. This is



1 avoided, in accordance with the present invention, by  
2 employment of the liquid metal reducing agent in  
3 considerable excess to transfer the heat to an external  
4 sink. The excess liquid metal reducing agent not only  
5 displaces the equilibrium in favour of the reaction; while  
6 part of the liquid metal reducing agent reacts and ceases to  
7 be metallic, the excess continues to act as a potent  
8 reductant but also acts as a highly efficient heat transfer  
9 medium, in situ, at the actual reactive zone where the heat  
10 is produced. A high yield of fully reduced desired metal is  
11 obtained by operating under these conditions, at a suitable  
12 reactor temperature. Partially this is because the strongly  
13 electro positive liquid metal reducing agent not only acts  
14 as a carrier and heat transfer medium but also as an  
15 unrestricted source of electrons by electronic conduction,  
16 once the covalent bonds of the halide of the desired metal  
17 are split. Substantially full reduction to desired metal  
18 occurs. There was no evidence that lesser reduction to  
19 undesired metal cations occurs. Working with excess liquid  
20 metal reducing agent in intimate contact with a compact  
21 <sup>form of reducible compound</sup> ~~phase~~, in contrast to a disperse vapour, is an important  
22 advance over prior art processes which at low temperatures  
23 have produced desired metal in low yields, due to partial  
24 reduction to lower halides.

25 If desired, heat might be removed from the reaction by  
26 circulating the liquid metal reducing agent to a cooling  
27 station but in general the conductivity of the liquid metal  
28 reducing agent will be effective in carrying heat to the  
29 wall of a reaction vessel from which heat may be removed.

30 In one instance at least portion of said liquid metal  
31 reducing agent is circulated between the reaction vessel and  
32 reaction product removal station whereby to convey reaction  
33 products away from said reaction vessel.

34 Preferably said liquid metal reducing agent is present  
35 in stoichiometric excess.

36 Preferably said desired metal that is produced is  
37 removed from said reaction with the liquid metal reducing  
38 agent and is thereafter separated from by-product halides of



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1 said liquid metal reducing agent and from the liquid metal  
2 reducing agent.

3 The operating pressure of the process should preferably  
4 be maintained by rare gas, e.g. argon, the current economic  
5 choice.

6 The process according to the invention may be carried  
7 out continuously and in such case excess liquid metal may be  
8 employed as a carrier to remove the reaction products at low  
9 temperature from the reaction vessel to suitable filters,  
10 screens, decantation vessels and/or centrifuges or vacuum  
11 distillation stages. A liquid slurry of the liquid metal  
12 reducing agent and reaction products will flow and can be  
13 pumped by known means.

14 The product salts (sodium chloride and/or potassium  
15 chloride) may be separated from the much heavier desired  
16 metal powder in a centrifuge, and the excess sodium,  
17 potassium or NaK alloy may then be centrifuged or filtered  
18 from these separately. Finally the residual NaK metal may be  
19 evaporated under high vacuum from the titanium powder after  
20 particle modification if desired, in a higher temperature  
21 loop.

22 In general, complete removal of liquid metal reducing  
23 agent halides from liquid metal reducing agent which is to  
24 be reused is not considered essential as such halides  
25 probably act as seeds for reaction initiation.

26 Anhydrous ammonia will be found useful in removing  
27 traces of liquid metal reducing agent from desired metal.

28 Preferably said reaction is initiated by liquefying  
29 said halide and, if necessary, a precursor material in solid  
30 form of said liquid metal reducing agent.

31 It is possible to pass liquid sodium metal  
32 countercurrent to by-product halides of said liquid metal  
33 reducing agent, <sup>whereby</sup> ~~whereby~~ to regenerate potassium metal from  
34 potassium chloride.

35 For high purity compact product, metal powder produced  
36 by the process of the present invention is preferably  
37 directly melted by the electron beam technique, which avoids  
38 the contamination experienced in the use of electric arcs on



1 water washed metal powder or that which has been exposed to  
2 the air. An electric arc must have a minimum amount of gas  
3 present to ionise, and will not operate in an ultra high  
4 vacuum that would strip all gases off hot surfaces. In  
5 conventional arc processes argon or helium atmospheres are  
6 employed but the absolute pressure necessary prevents good  
7 stripping of air and water vapour from the washed metal  
8 powder.

9 Electron beam melting is generally becoming the  
10 preferred compacting means in rare and contaminatable metal  
11 technology, for example that of titanium, hafnium,  
12 zirconium, tantalum and tungsten.

13 Thus in a preferred embodiment of the invention, metal  
14 powder from which the residual NaK alloy has been  
15 evaporated, is fed directly into the melting electron beam  
16 without ever having been exposed to air or water. In these  
17 circumstances small particle size is advantageous. Also  
18 electroslag melting may be applicable.

19 In another embodiment powder suitably conditioned in a  
20 hot loop may be released to ambient and handled  
21 conventionally for use in powder metallurgy or for hydrogen  
22 storage as hydride. Treatment with an alcohol or ketone has  
23 been found to reduce and in some cases eliminate pyrophoric  
24 problems.

25 Because liquid sodium reduces potassium from its molten  
26 salts (cf vice versa in aqueous media), no difficulty in  
27 keeping potassium captive in the system is anticipated. In  
28 one proposed embodiment of the invention, for continuous  
29 production of titanium, liquid Na metal from an electrolytic  
30 reduction cell would enter the process counter current to  
31 outgoing mixed product NaCl and KCl stream. This counter  
32 current contacting, with sufficient heat and mass transfer  
33 stages, would both retain the K in the system and conserve  
34 the heat.

35 Then overall the feed to the process would be,  $TiCl_4$   
36 and Na metal and the products be Ti metal and NaCl which  
37 latter could be recycled directly to an electrolytic cell  
38 from which in turn  $Cl_2$  would be available either to an



1 integrated  $\text{TiCl}_4$  production plant or for sale according to  
2 economics of procurement of  $\text{TiCl}_4$  and titanium source  
3 materials, e.g. rutile plus carbon, at the plant site. For  
4 economic reasons site melted Na brought into the site, may  
5 be better than recycle to an integrated electrolytic cell,  
6 without affecting the generality of the principle of captive  
7 K, which essentially removes its cost from the economics of  
8 production, this being essentially tied to  $\text{TiCl}_4$  and Na in  
9 and  $\text{Ti} + \text{NaCl}$  out of the essential process. Similar  
10 considerations apply to other desired metals.

11 EXAMPLE 1

12 Titanium metal was recovered from  $\text{TiCl}_4$  by reaction  
13 with a large excess of NaK alloy.

14 The apparatus incorporated means for evacuating the  
15 system to below 10 microns of mercury; a supply of inert  
16 gas; the means for external heating and cooling a reactor,  
17 with a heat transfer medium inert to NaK. The reactor was  
18 made of pyrex glass so that the reaction mixture was clearly  
19 visible. A stirrer totally isolated from ambient was built  
20 into the reactor, and means for sampling while stirring  
21 while under inert gas or vacuum were provided. Safety of  
22 operation was a paramount consideration.

23 The stirrer was adjustable and made of nickel tubing,  
24 as it is known that nickel is an inert reaction vessel  
25 material for the preparation of titanium from its chlorides.  
26 As autocatalysis may be important in the mechanism,  
27 facilities were provided for both nickel and titanium  
28 propellers on the stirrer.

29 The reactor was made of pyrex glass, surrounded by a  
30 pyrex glass jacket through which high flash point, low  
31 viscosity oil was pumped to either heat or cool the  
32 reactants. The jacket, in particular the base, was designed  
33 to maintain high heat transfer rates at the vessel walls.  
34 Inside the reactor, the stirred liquid NaK alloy itself  
35 constituted an excellent heat transfer medium. On one side  
36 of the vessel was provided a connection to a burette  
37 containing  $\text{TiCl}_4$ , and on the other side a vent to a mercury  
38 lute. A sampling probe was also provided.



1 A thermocouple was connected into the cooling systm at  
2 the point where the oil leaves the glass jacket surrounding  
3 the reactor.

4 The lute provided was adapted to vent to atmosphere any  
5 pressure surge which may occur in the system, yet allow a  
6 high vacuum to be applied to the system.

7 Argon gas was used as the protective gas, as is  
8 customary the preparation of titanium, but facilities for  
9 using nitrogen were also built into the system. The argon  
10 used was a commercially pure grade, and was purified of any  
11 traces of water vapour and oxygen before admission following  
12 evacuation.

13 The titanium tetrachloride used was laboratory reagent  
14 grade, which was distilled in an atmosphere of nitrogen  
15 before use, the boiling range  $133^{\circ}\text{C}$  to  $136^{\circ}\text{C}$  being  
16 collected.

17 60/40 mole % NaK sodium-potassium alloy was prepared. 30  
18 g (1020 millimoles) of the alloy was charged into the  
19 reactor via a No. 3 porous filter disc, under the cover of  
20 argon gas, and the tetrachloride was placed in a burette  
21 which had a fitting to connect it to the reactor.

22 The stirrer was set running and 2.00 ml. (18  
23 millimoles) of  $\text{TiCl}_4$  was added to the alloy. The reaction  
24 mixture was stirred vigorously. The top layer of alloy  
25 became darker and went through a wide range of colours:  
26 gold, blue, pink and green all being noticeable. Then  
27 another 1.20 ml (11 millimoles) of  $\text{TiCl}_4$  was added and once  
28 again many colours were visible, then 70 seconds after the  
29 addition, there was a flash of light, and a recorder showed  
30 a rapid  $0.8^{\circ}\text{C}$  increase in the temperature of cooling fluid  
31 from about  $25^{\circ}\text{C}$ . A dark grey substance was now seen inside  
32 the apparatus intermixed with the liquid metal. There was  
33 evidence of a considerable increase in the viscosity of the  
34 excess liquid metal.

35 The whole system was evacuated to remove any remaining  
36  $\text{TiCl}_4$  (none was found in subsequent tests on the cold trap  
37 washings). To facilitate analysis of the products, two lots  
38 of 25 ml. of ethanol (436 millimoles each) were added to

1 destroy the alloy.

2 When all the alloy was destroyed, suction was applied  
3 to a sample probe inserted into the reactor and as much  
4 material as possible was withdrawn into the filter. The  
5 solid's were filtered and washed with ethanol and then dried  
6 under vacuum. The reaction vessel also contained a quantity  
7 of rather finer solids and these were also collected and  
8 washed with ethanol, but kept separate from the coarser  
9 samples. The two samples were extracted with hot water, and  
10 after drying, the mass of water-insoluble material was 1.53  
11 g, 1.12 g from the coarse sample and 0.41 g from the fine  
12 sample.

13 Metallurgical examination indicated that both samples  
14 after the above treatment comprised non-pyrophoric titanium.

15 For purpose of examination, they were dissolved in hot  
16 dilute sulphuric acid, precipitated with ammonia and ignited  
17 to  $TiO_2$ . The yield was close to theoretical.

18 EXAMPLE II

19 The procedure of Example I was repeated excepting that  
20  $Al_2Cl_3$  was used in lieu of  $TiCl_4$ .

21 Aluminium metal was produced although yields were low  
22 and reaction times long probably due to the fact that the  
23  $Al_2Cl_3$  remained in solid state throughout the process; the  
24 apparatus used being incapable of holding the pressure  
25 necessary to liquefy  $Al_2Cl_3$  under the temperatures that were  
26 practical.

27 EXAMPLE III

28 While the process exemplified in Example II proved the  
29 process of this invention as applicable to aluminium,  
30 further experiment was made to improve yields by conducting  
31 the process inside a sealed bomb so as to ensure  
32 liquefaction of  $Al_2Cl_3$ .

33 30g of a 60/40 mole % NaK sodium - potassium alloy was  
34 charged into a bomb under inert atmosphere conditions and  
35 10gm of dry freshly prepared  $Al_2Cl_3$  was also charged into the  
36 bomb under inert atmosphere conditions.

37 The bomb was sealed and heated to  $300^\circ C$  and maintained  
38 at that temperature for 15m.



1 After cooling, the bomb was unsealed under an inert  
2 atmosphere and the NaK alloy was destroyed and product metal  
3 was extracted similarly as in Example I.

4 A yield of aluminium of 80% of theoretical was  
5 obtained.

6 This example indicates the desirability of the halide  
7 being in liquid phase.

8 By the use of the exemplary processes we can provide a  
9 pure metal such as titanium, aluminium or an alloy such as  
10 TiFe suitable for the new hydride storage technology or  
11 other metals or mixtures of metals for which truly anhydrous  
12 halides are preferred.

The claims defining the invention are as follows:-

1. A method of obtaining a desired metal selected from the group consisting of metals capable of existing in the form of a compound capable of being reduced with a liquid metal reducing agent which comprises a reaction comprising contacting such a compound of said desired metal in substantially compact form with a liquid metal reducing agent being sodium and potassium metals at a temperature not greater than the boiling point or the sublimation point of the compound at the pressure of the reaction whereby to obtain said desired metal.
2. A method as claimed in claim 1, wherein said compound is a covalent halide.
3. A method as claimed in claim 1, wherein said desired metal is selected from the group consisting of titanium, aluminium, iron, manganese, hafnium, zirconium, tantalum, vanadium, uranium and tungsten.
4. A method of obtaining a desired metal selected from the group consisting of titanium, aluminium, iron, manganese, hafnium, zirconium, tantalum, vanadium, uranium and tungsten which comprises a reaction comprising contacting a halide of said desired metal in substantially compact form with a liquid metal reducing agent being sodium and potassium metals at a temperature not greater than the boiling point or the sublimation point of the compound at the pressure of the reaction whereby to obtain said desired metal.
5. A method as claimed in claim 4, wherein said desired metal is titanium.



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6. A method as claimed in claim 4, wherein said desired metal is aluminium.
7. A method as claimed in claim 4, wherein the halide is an anhydrous halide.
8. A method as claimed in claim 4, wherein the halide is in liquid phase.
9. A method as claimed in claim 8, wherein the halide is in solution.
10. A method as claimed in claim 8, wherein the halide is in suspension.
11. A method as claimed in claim 4, wherein the halide is in liquefied form.
12. A method as claimed in claim 4, wherein the halide is in solid form.
13. A method as claimed in any preceding claim wherein said liquid metal reducing agent comprises a mixture of metals containing a Group I metal.
14. A method as claimed in claim 13, wherein said liquid metal reducing agent is a mixture of sodium and potassium alloy.
15. A method as claimed in claim 13, wherein said liquid metal reducing agent addition alloy includes at least one of calcium and magnesium.
16. A method as claimed in any preceding claim wherein said reaction is conducted under substantially anhydrous conditions.
17. A method as claimed in claim 4, wherein said reaction is conducted at a temperature and pressure such that the halide and said liquid metal reducing agent are maintained in liquefied form.
18. A method as claimed in claim 17, wherein said reaction is conducted at a temperature such that solid by-product halides of said liquid metal reducing agent are formed.
19. A method as claimed in any preceding claim wherein said reaction is conducted under substantially oxygen free conditions.



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20. A method as claimed in any preceding claim which is conducted in a reaction vessel and wherein at least a portion of said liquid metal reducing agent is circulated between the reaction vessel and a reaction products removal station whereby to convey <sup>reaction</sup> ~~reaction~~ products away from said reaction vessel.
21. A method as claimed in any preceding claim wherein said liquid metal reducing agent is present in stoichiometric excess.
22. A method as claimed in any preceding claim wherein said reaction is effected under an inert atmosphere.
23. A method as claimed in claim 4, wherein said desired metal that is produced is removed from said reaction with the liquid metal reducing agent and is thereafter separated from by-product halides of said liquid metal reducing agent and from the liquid metal reducing agent.
24. A method as claimed in any preceding claim wherein said reaction is initiated by liquefying said halide and if necessary a precursor material in solid form of said liquid metal reducing agent.
25. A method as claimed in claim 14, comprising passing liquid sodium metal countercurrent to by-product halides of said liquid metal reducing agent whereby to regenerate potassium metal from potassium chloride.
26. A method of producing a metal substantially as hereinbefore described with reference to any one of the Examples.

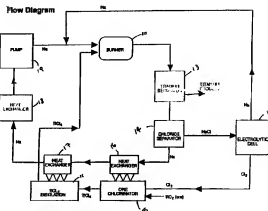
DATED this 30th day of June 1989

THE UNIVERSITY OF MELBOURNE  
By Its Patent Attorneys

A. TATLOCK & ASSOCIATES  
Fellows Institute of Patent  
Attorneys of Australia



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(51) Int.Cl.<sup>6</sup> C22B 5/00, C22B 34/12, C22C 1/06, C22B 34/00, C22B 21/04, C22C 14/00

(30) 1994/08/01 (08/283,358) US

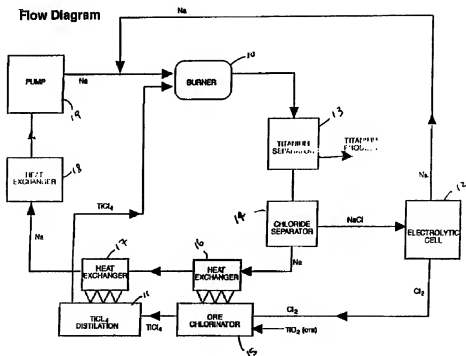
(54) **PROCEDE DE PRODUCTION DE METAUX ET D'AUTRES ELEMENTS**

(54) **METHOD OF MAKING METALS AND OTHER ELEMENTS**

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(87) 1996/02/15

(45) 2001/04/10



(57) Procédé de production d'un élément non métallique, d'un métal ou bien d'un alliage de ces derniers à partir d'un halogénure ou de mélanges d'halogénures. Selon ce procédé on met en contact l'halogénure ou le mélange d'halogénures avec un écoulement de métal alcalin liquide, ou de métal alcalino-terreux ou encore de mélanges de ces derniers dans une quantité suffisante pour que l'halogénure se transforme en un non métal, en

(57) A method of producing a non-metal element or a metal or an alloy thereof from a halide or mixtures thereof. The halide or mixtures thereof are contacted with a stream of liquid alkali metal or alkaline earth metal or mixtures thereof in sufficient quantity to convert the halide to the non-metal or the metal or alloy and to maintain the temperature of the reactants at a temperature lower than the lesser of the boiling point of the alkali or





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(86) 1995/07/25

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(45) 2001/04/10

un métal ou en un alliage et pour maintenir la température des réactants à une température inférieure à la plus basse température d'ébullition du métal alcalin ou du métal alcalino-terreux à la pression atmosphérique ou la température de frittage du non métal, du métal ou de l'alliage produit. On décrit un procédé en continu s'appliquant tout particulièrement au titane.

alkaline earth metal at atmospheric pressure or the sintering temperature of the produced non-metal or metal or alloy. A continuous method is disclosed, particularly applicable to titanium.

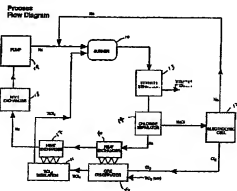




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: METHOD OF MAKING METALS AND OTHER ELEMENTS



(57) Abstract

A method of producing a non-metal element or a metal or an alloy thereof from a halide or mixtures thereof. The halide or mixtures thereof are contacted with a stream of liquid alkali metal or alkaline earth metal or mixtures thereof in sufficient quantity to convert the halide to the non-metal or the metal or alloy and to maintain the temperature of the mixtures at a temperature lower than the lower of the boiling point of the alkali or alkaline earth metal or atmospheric pressure or the melting temperature of the produced non-metal or metal or alloy. A continuous method is disclosed, particularly applicable to titanium.

### Background of the Invention

This invention relates to the production of elemental material from the halides thereof and has particular applicability to those metals and non-metals for which the reduction of the halide to the element is exothermic. Particular interest exists for titanium and the present invention will be described with particular reference to titanium but is applicable to other metals and non-metals such as Al, As, Sb, Be, B, Ta, Ge, V, Nb, Mo, Ga, Ir, Os, U and Re, all of which produce significant heat upon reduction from the halide to the metal. For the purposes of this application, elemental materials include those metals and non-metals listed above or in Table 1.

At present titanium production is by reduction of titanium tetrachloride, which is made by chlorinating relatively high-grade titanium dioxide ore. Ores containing rutile can be physically concentrated to produce a satisfactory chlorination feed material; other sources of titanium dioxide, such as ilmenite, titaniferous iron ores and most other titanium source materials, require chemical beneficiation.

The reduction of titanium tetrachloride to metal has been attempted using a number of reducing agents including hydrogen, carbon, sodium, calcium, aluminum and magnesium. The magnesium reduction of titanium tetrachloride has proved to be a commercial method for producing titanium metal. However, the resultant batch process requires significant material handling with resulting opportunities for contamination and also in

quality variation from batch to batch. The greatest potential for decreasing production cost is the development of a continuous reduction process with attendant reduction in material handling.

There is a strong demand for the development of a process that enables continuous economical production of titanium powder suitable for use without additional processing for application to powder metallurgy or vacuum-arc melting to ingot form. The Kroll process and the Hunter process are the two present day methods of producing titanium commercially.

In the Kroll process, titanium tetrachloride is chemically reduced by magnesium at about 1000°C. The process is conducted in a batch fashion in a metal retort with an inert atmosphere, either helium or argon. Magnesium is charged into the vessel and heated to prepare a molten magnesium bath. Liquid titanium tetrachloride at room temperature is dispersed dropwise above the molten magnesium bath. The liquid titanium tetrachloride vaporizes in the gaseous zone above the molten magnesium bath. A surface reaction occurs to form titanium and magnesium chloride. The Hunter process is similar to the Kroll process, but uses sodium instead of magnesium to reduce the titanium tetrachloride to titanium metal and produce sodium chloride.

For both processes, the reaction is uncontrolled and sporadic and promotes the growth of dendritic titanium metal. The titanium fuses into a mass that encapsulates some of the molten magnesium (or sodium) chloride. This fused mass is

called titanium sponge. After cooling of the metal retort, the solidified titanium sponge metal is broken up, crushed, purified and then dried in a stream of hot nitrogen. Powder titanium is usually produced through grinding, shot casting or centrifugal processes. A common technique is to first cause the titanium to absorb hydrogen to make the sponge brittle to facilitate the grinding process. After formation of the powder titanium hydride, the particles are dehydrogenated to produce a usable product. The processing of the titanium sponge into a usable form is difficult, labor intensive, and increases the product cost by a factor of two to three.

During these processing steps, some sponge particles as large as several centimeters in size may be ignited in air and are thereby converted to titanium oxynitride, which is usually not destroyed during the melting operation. The resulting inclusions of hard material within the titanium metal parts have been identified as causing disastrous failures of jet engine parts, leading to crashes of aircraft.

The processes discussed above have several intrinsic problems that contribute heavily to the high cost of titanium production. Batch process production is inherently capital and labor intensive. Titanium sponge requires substantial additional processing to produce titanium in a usable form, increasing cost, increasing hazard to workers and exacerbating batch quality control difficulties. Neither process utilizes the large exothermic energy reaction, requiring substantial energy input for titanium production (approximately 6 kw-hr/kg

product metal). In addition, the processes generate significant production wastes that are of environmental concern.

#### Summary of the Invention

Accordingly, an object of the present invention is to provide a method and system for producing non-metals or metals or alloys thereof which is continuous having significant capital and operating costs advantages over existing batch technologies.

Another object of the present invention is to provide a method and system for producing metals and non-metals from the exothermic reduction of the halide while preventing the metal or non-metal from sintering onto the apparatus used to produce same.

Still another object of the invention is to provide a method and system for producing non-metal or metal from the halides thereof wherein the process and system recycles the reducing agent, thereby substantially reducing the environmental impact of the process.

The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, and particularly pointed out in the appended claims, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

**Brief Description of the Drawings**

For the purpose of facilitating an understanding of the invention, there is illustrated in the accompanying drawings a preferred embodiment thereof, from an inspection of which, when considered in connection with the following description, the invention, its construction and operation, and many of its advantages should be readily understood and appreciated.

FIGURE 1 is a process flow diagram showing the continuous process for producing as an example titanium metal from titanium tetrachloride;

FIG. 2 is a heat balance flow sheet for a process wherein the reactants exiting the burner are about 300°C; and

FIG. 3 is an energy balance for a process in which the reactants exits the burner at about 850°C; and

FIG. 4 is a schematic illustration of the prior art Kroll or Hunter process.

**Detailed Description of the Invention**

The process of the invention may be practiced with the use of any alkaline or alkaline earth metal depending upon the transition metal to be reduced. In some cases, combinations of an alkali or alkaline earth metals may be used. Moreover, any halide or combinations of halides may used with the present invention although in most circumstances chlorine, being the cheapest and most readily available, is preferred. Of the alkali or alkaline earth metals, by way of example, sodium will be chosen not for purposes of limitation but merely purposes of illustration, because it is cheapest and preferred, as has chlorine been chosen for the same purpose.

Regarding the non-metals or metals to be reduced, it is possible to reduce a single metal such as titanium or tantalum zirconium, selected from the list set forth hereafter. It is also possible to make alloys of a predetermined composition by providing mixed metal halides at the beginning of the process in the required molecular ratio. By way of example, Table 1 sets forth heats of reaction per gram of sodium for the reduction of non-metal or metal halides applicable to the inventive process.

Table 1

FEEDSTOCK	HEAT kJ/g
$\text{TiCl}_4$	10
$\text{AlCl}_3$	9
$\text{SbCl}_3$	14
$\text{BeCl}_2$	10
$\text{BCl}_3$	12
$\text{TaCl}_5$	11
$\text{VCl}_4$	12
$\text{NbCl}_5$	12
$\text{MoCl}_4$	14
$\text{GaCl}_3$	11
$\text{UF}_6$	10
$\text{ReF}_6$	17

The process will be illustrated, again for purposes of illustration and not for limitation, with a single metal titanium being produced from the tetrachloride.



A summary process flowsheet is shown in Figure 1. Sodium and titanium tetrachloride are combined in a burner reaction chamber 10 where titanium tetrachloride vapor from a source thereof in the form of a distillation column 11 is injected into a flowing sodium stream from a source (not shown) thereof. Make up sodium is produced in an electrolytic cell 12. The reduction reaction is highly exothermic, forming molten reaction products of titanium and sodium chloride. The molten reaction products are quenched in the bulk sodium stream. Particle sizes and reaction rates are controlled by metering of the titanium tetrachloride vapor flowrate, dilution of the titanium tetrachloride vapor with an inert gas, such as He or Ar, and the sodium flow characteristics and mixing parameters where the burner includes concentric nozzles having an inner nozzle for the  $TiCl_4$  and the outer nozzle for the liquid sodium, the gas is intimately mixed with the liquid and the resultant temperature, significantly affected by the heat of reaction, can be controlled by the quantity of sodium and maintained below the sintering temperature of the produced metal, such as titanium or about 1000°C.

The bulk sodium stream then contains the titanium and sodium chloride reaction products. These reaction products are removed from the bulk sodium stream by conventional separators 13 and 14 such as cyclones or particulate filters. Two separate options for separation of the titanium and the sodium chloride exist.

The first option removes the titanium and sodium chloride products in separate steps. This is accomplished by maintaining the bulk stream temperature such that the titanium is solid but the sodium chloride is molten through control of the ratio of titanium tetrachloride and sodium flowrates to the burner 10. For this option, the titanium is removed first, the bulk stream cooled to solidify the sodium chloride, then the sodium chloride is removed from separator 14. In this option, the process heat for titanium tetrachloride distillation would be removed from the bulk stream immediately after the titanium separator 13.

In the second option for reaction product removal, a lower ratio of titanium tetrachloride to sodium flowrate would be maintained in the burner 10 so that the bulk sodium temperature would remain below the sodium chloride solidification temperature. For this option, titanium and sodium chloride would be removed simultaneously. The sodium chloride and any residual sodium present on the particles would then be removed in a water-alcohol wash.

Following separation, the sodium chloride is then recycled to the electrolytic cell 12 to be regenerated. The sodium is returned to the bulk process stream for introduction to burner 10 and the chlorine is used in the ore chlorinator 15. It is important to note that while both electrolysis of sodium chloride and subsequent ore chlorination will be performed using technology well known in the art such integration and recycle of the reaction byproduct is not

possible with the Kroll or Hunter process because of the batch nature of those processes and the production of titanium sponge as an intermediate product. Operators of the Kroll and Hunter processes purchase titanium tetrachloride for use in the manufacture of titanium. The integration of these separate processes enabled by the inventive chemical manufacturing process has significant benefits with respect to both improved economy of operation and substantially reduced environmental impact achieved by recycle of waste streams.

Chlorine from the electrolytic cell 12 is used to chlorinate titanium ore (rutile, anatase or ilmenite) in the chlorinator 15. In the chlorination stage, the titanium ore is blended with coke and chemically converted in the presence of chlorine in a fluidized-bed or other suitable kiln chlorinator 15. The titanium dioxide contained in the raw material reacts to form titanium tetrachloride, while the oxygen forms carbon dioxide with the coke. Iron and other impurity metals present in the ore are also converted during chlorination to their corresponding chlorides. The titanium chloride is then condensed and purified by means of distillation in column 11. With current practice, the purified titanium chloride vapor would be condensed again and sold to titanium manufacturers; however, in this integrated process, the titanium tetrachloride vapor stream is used directly in the manufacturing process.

After providing process heat for the distillation step in heat exchanger 17, the temperature of the bulk process stream is adjusted to the desired temperature for the burner 10

at heat exchanger 18, and then combined with the regenerated sodium recycle stream, and injected into the burner. It should be understood that various pumps, filters, traps, monitors and the like will be added as needed by those skilled in the art.

Referring now to Figures 2 and 3, there is disclosed flow diagrams, respectively, for a low temperature process in Fig. 2 and a high temperature process in Fig. 3. The principal differences are the temperatures at which the sodium enters and leaves the burner 10. Like numbers have been applied for like equipment, the purpose of which was explained in Figure 1. For instance in Fig. 2 for the low temperature process, the sodium entering the burner 10 is at 200°C having a flow rate of 38.4 kilograms per minute. The titanium tetrachloride from the boiler 11 is at 2 atmospheres and at a temperature of 164°C, the flow rate through line 15a being 1.1 kg/min. Pressures up to 12 atmospheres may be used, but it is important that back flow be prevented, so an elevated at pressure of at least 2 atmospheres is preferred to ensure that flow through the burner nozzle is critical or choked. In all aspects, for the process of Figures 1 as well as the processes of Figures 2 and 3, it is important that the titanium that is removed from the separator 13 be at or below and preferably just below the sintering temperature of titanium in order to preclude and prevent the solidification of the titanium on the surfaces of the equipment, which is one of the fundamental difficulties with the processes commercially used presently. By maintaining the temperature of the titanium metal below the sintering

temperature of titanium metal, the titanium will not attach to the walls of the equipment as it presently does and, therefore, the physical removal of same will be obviated. This is an important aspect of this invention and is obtained by the use of sufficient Na metal or diluent gas or both to control the temperature of the elemental (or alloy) product.

By way of interest, batch processes now in use require that the titanium sponge be jackhammered from the collection vessel and considering the hardness of the sponge, is no mean task.

The high-temperature process illustrated in Fig. 3 shows that the temperature at which the sodium enters the boiler is at 750°, having a flow rate of about 33.4 kg.

The temperature of product from the burner in the low temperature process of Fig. 2 is about 300°C whereas the high temperature process is at about 850°C. It is clear that even at the high temperature process, the titanium is well below the sintering temperature which is approximately 1000°C, thereby ensuring that the shortcomings of the present day process are avoided. The heat exchangers in both Figs. 2 and 3 are identified by the numeral 20 although the values of the power removed is different for the processes of Fig. 2 (low temperature) and Fig. 3 (high temperature), due in part because of the placement of the heat exchanger 20 in the high temperature process prior to the separation of sodium chloride while in the low temperature process, the heat exchanger 20 is subsequent to the separation of sodium chloride resulting in

different power outputs as indicated. In both flow diagrams of Figs. 2 and 3, sodium make-up is indicated by the line 12A and this may come from an electrolytic cell 12 or some other source of sodium entirely different. In other aspects, both Figures 2 and 3 are illustrative of the types of design parameters which may be used to produce titanium metal in a continuous process which avoids the problems inherent in the batch process presently in use commercially.

The invention has been illustrated by reference to titanium alone and titanium tetrachloride as a feedstock, in combination with sodium as the reducing metal. However, it should be understood that the foregoing was for illustrative purposes only and the invention clearly pertains to those metals and non-metals in Table 1, which of course include the fluorides of uranium and rhenium and well as other halides such as bromides. Moreover, sodium while being the preferred reducing metal because of cost and availability, is clearly not the only available reductant. Lithium, potassium as well as calcium and other alkaline earth metals are available and thermodynamically feasible. It is well within the skill of the art to determine from the thermodynamic Tables which metals are capable of acting as a reducing agent in the foregoing reactions, the principal applications of the process being to those reactions which are highly exothermic as illustrated in Table 1 when the chloride or halide is reduced to the metal. Moreover, it is well within the skill of the art and it is contemplated in this invention that alloys can be made by the

process of the subject invention by providing a suitable halide feed in the molecular ratio of the desired alloy.

While there has been disclosed what is considered to be the preferred embodiment of the present invention, it is understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method of producing an elemental material or an alloy thereof from a halide vapor of the elemental material or a halide vapor of the alloy comprising submerging the halide vapor in flowing liquid alkali metal or liquid alkaline earth metal or mixtures thereof to convert the halide vapor to elemental material or an alloy wherein the conversion of the halide vapor to the elemental material or the alloy is exothermic.

2. The method of claim 1, wherein the elemental material is one or more of Ti, Al, Sb, Be, B, Ga, Mo, Nb, Ta, Zr, and V.

3. The method of claim 1, wherein the elemental material is one or more of Ir, Os, Re and U.

4. The method of claim 1, wherein the alkali metal is one or more of Na, K and Li.

5. The method of claim 1, wherein the alkaline earth metal is one or more of Ca, Sr and Ba.

6. The method of claim 1, wherein the halide is one or more of Cl, Br and F.

7. The method of claim 1, wherein the alkali metal is one or more of Na and K, the alkaline earth metal is one or more of Ca and Ba and the halide is one or more of Cl and Br.



8. The method of claim 1, wherein the halide vapor is supplied at a pressure sufficient to maintain sonic flow.

9. The method of claim 1 and further comprising adding an inert gas to the halide vapor.

10. The method of claim 9, wherein the inert gas is Ar or He.

11. The method of claim 1, wherein the elemental material or alloy produced does not sinter.

12. A method of continuously producing a non-metal or a metal or an alloy thereof comprising, providing a supply of halide vapor of the metal or non-metal or mixtures thereof, providing a supply of flowing liquid alkali or alkaline earth metal or mixtures thereof, introducing the halide vapor submerged in the flowing liquid alkali metal or alkaline earth metal or mixtures thereof to produce a powder of the non-metal or metal or alloy thereof and a halide of the alkali or alkaline earth metal, wherein the reduction of the halide to the metal or non-metal is exothermic, separating the powder from the alkali metal halide or the alkaline earth metal halide, separating the alkali metal halide or the alkaline earth metal halide into its constituent parts, cooling and recycling the alkali metal or the alkaline earth metal to react with additional halide vapor.

13. The method of claim 12, wherein the halide has a boiling point less than 400°C.

14. The method of claim 13, wherein the halide vapor flows through an inner nozzle of concentric inner and

outer nozzles with the liquid alkali or alkaline earth metal flowing through the annulus formed by said inner and outer nozzles, the vapor flow being sonic.

15. The method of claim 14, wherein the halide vapor is one or more of  $\text{TiCl}_4$ ,  $\text{VCl}_4$ ,  $\text{NbCl}_5$ ,  $\text{MoCl}_4$ ,  $\text{GaCl}_3$ ,  $\text{UF}_6$ ,  $\text{ReF}_6$ .

16. The method of claim 12, wherein the halide is one or more of Br and Cl.

17. A method of producing an elemental material or alloys thereof selected from the class consisting of Ti, Al, Sb, Be, B, Ga, Mo, Nb, Ta, Zr, and V from a vapor halide of the elemental material or mixtures of the elemental materials comprising introducing the vapor halide or mixtures thereof by submerged injection into flowing liquid alkali or alkaline earth metal or mixtures thereof at a velocity not less than the sonic velocity of the halide vapor, the liquid alkali or alkaline earth metal or mixtures thereof being present in a quantity effective to convert the halide vapor or mixtures thereof to elemental material or an alloy thereof.

18. A method of producing Ti powder from a source of  $\text{TiCl}_4$  vapor, comprising introducing the  $\text{TiCl}_4$  vapor submerged in a flowing stream of liquid Na to produce Ti powder and separating the Ti powder from the liquid Na.

19. A method of continuously producing a non-metal or a metal or an alloy thereof comprising, providing a supply of halide vapor of the metal or non-metal or mixtures thereof, providing a supply of flowing liquid alkali or alkaline earth metal or mixtures thereof, introducing the halide vapor

submerged in the flowing liquid alkali metal or alkaline earth metal or mixtures thereof to produce a powder of the non-metal or metal or alloy thereof and a halide of the alkali or alkaline earth metal, said alkali or alkaline earth metal being present in sufficient quantities in excess of the stoichiometric quantity necessary to reduce the halide vapor, to quench the alkali metal halide or the alkaline earth metal halide below the sintering temperature of the non-metal or metal or alloy thereof, to recover heat from the excess alkali or alkaline earth metal, to separate the alkali metal halide or the alkaline earth metal halide into its constituent parts, to recycle the alkali metal or the alkaline earth metal and recycling the alkali metal or the alkaline earth metal to react with additional halide vapor, and to recycle halogen vapor to react with ore of the metal or non-metal.

20. The method of claim 1, wherein the halide vapor or mixtures thereof is submerged in liquid alkali metal or liquid alkaline earth metal or mixtures thereof by introducing the halide vapor into the liquid through a submerged injector.

21. The method of claim 20, wherein the injector is a nozzle.

22. The method of claim 12, wherein the reaction takes place in equipment suitable therefor and there is an excess of the alkaline metal or alkaline earth metal over the stoichiometric quantity needed to react with the halide vapor such that the temperature of the powder of the non-metal or metal or alloy produced is controlled to prevent the powder from depositing on the equipment.

23. The method of claim 12, wherein the reaction takes place in equipment suitable therefor and the temperature of the reactants is maintained low enough that the elemental metal or alloy reaction products is quenched by contact with the alkali metal or alkaline earth metal.

24. The method of claim 12, and further comprising contacting the halide obtained from separating the alkali metal halide or alkaline earth metal halide into its constituent parts with ore of the elemental metal or alloy.

25. The method of claim 17, wherein the elemental material or alloy is produced in a continuous process.

26. The method of claim 17, wherein the halide is  $TiCl_4$ , the alkali metal is Na and the temperature of the liquid Na away from where the halide vapor is introduced is maintained at about 300°C.

27. The method of claim 26, wherein the liquid Na is present in sufficient excess to quench Ti powder upon production thereof to reduce the temperature of the Ti powder below the sintering temperature of Ti.

28. The method of claim 19, wherein the halide is the chloride of one or more of Ti or Zr.

29. The method of claim 28, wherein the alkali or alkaline earth metal is Na or Mg.

30. The method of claim 29, wherein the alkali or alkaline earth metal is present as a flowing stream and the chloride vapor is introduced by injection thereinto.

31. The method of claim 30, wherein at least some of the recovered heat is used for power generation.

32. The method of claim 19, wherein the halide is  $\text{TiCl}_4$  and the alkali or alkaline earth metal is Na.

33. The method of claim 18, wherein the  $\text{TiCl}_4$  vapor is introduced into the flowing stream of liquid Na by injection.

34. The method of claim 18, wherein the  $\text{TiCl}_4$  vapor is introduced at sonic velocity into the flowing Na stream.

35. The method of claim 18, wherein the flowing stream of Na is present in excess over the stoichiometric quantity needed to react with the  $\text{TiCl}_4$  vapor such that the Ti powder produced does not sinter.

36. A method of producing Ti powder from a source of  $\text{TiCl}_4$  vapor, comprising introducing the  $\text{TiCl}_4$  vapor at a velocity not less than the sonic velocity of the vapor submerged in liquid Na to product Ti powder and separating the Ti powder from the liquid Na.

37. The method of claim 36 wherein the liquid Na is maintained at a temperature of about  $300^\circ\text{C}$  except where the  $\text{TiCl}_4$  reacts with the liquid Na.

38. The method of claim 19 wherein the halide vapor is introduced at a velocity equal to or greater than the sonic velocity of the halide vapor.

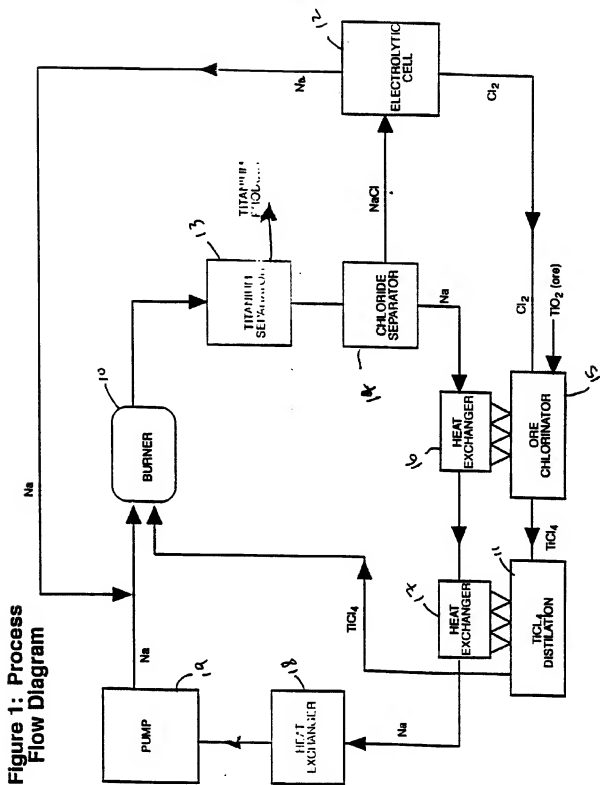
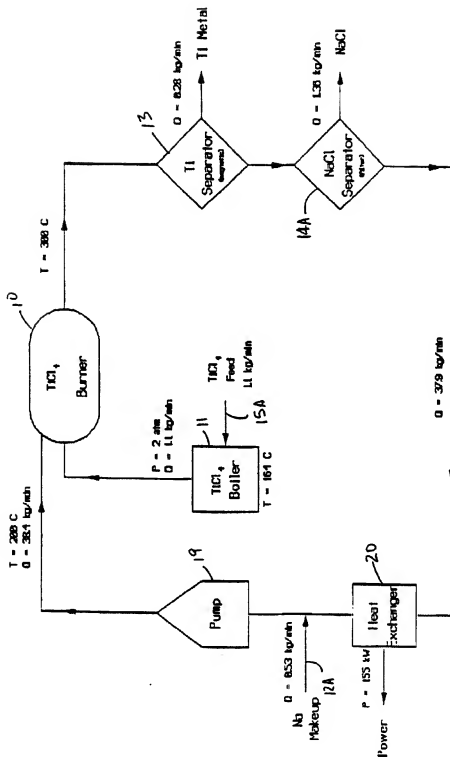


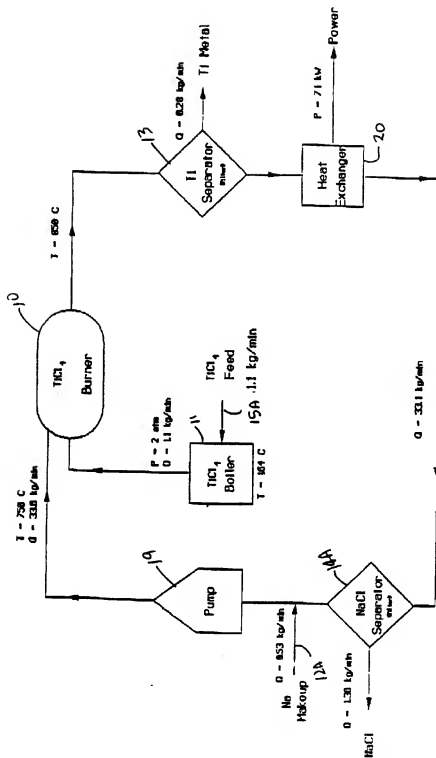
Figure 2



## Low Temperature Process

basals : critical flow through 5 mm nozzle

Figure 3



## High Temperature Process

basis: critical flow through 5 mm nozzle



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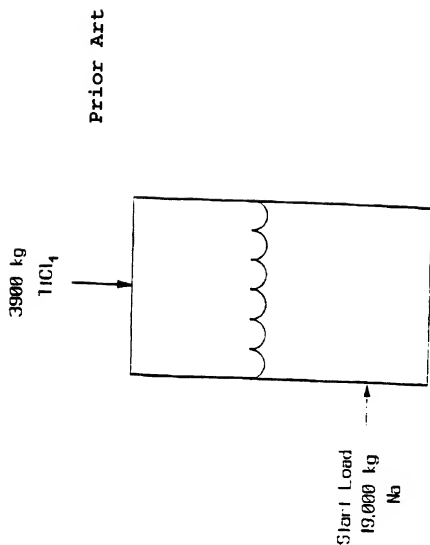


Figure 4

## Batch Process

basis : 150 mtpy (same as continuous process)

EUROPEAN PATENT APPLICATION

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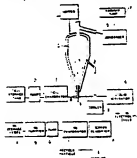
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(10) Method for producing a metal from its halide.

EP 0 298 698 A1  
 (11) A method for producing metal by the reduction of a metal halide by a reducing metal agent capable of continuously producing homogeneous metal of high purity. In the method, particles of the same metal as the metal to be produced are charged into a reaction vessel and the metal halide and the reducing metal agent both in vapour form, are ejected upwards into the reaction vessel from its lower portion to form a fluidized bed of the metal particles in the vessel. The reducing reaction between the two vapours takes place on the surface of the metal particles at a temperature below the melting point of the metal product and at a pressure below a vapour pressure of each of the reducing metal agent and

the metal halide at that temperature, resulting in depositing and growing the metal product on the surface of the particles.



## METHOD FOR PRODUCING A METAL FROM ITS HALIDE

The present invention relates to a method for producing metal from a metal halide, and more particularly to a method for the production of a metal by the reduction of its metal halide by a reducing metal agent.

A conventionally known method for producing a metal by the reduction of its metal halide comprises the so-called Kroll process, which is particularly suitable for the production of titanium. Unfortunately, this process has a disadvantage in causing the metal product, for example, titanium to become firmly adhered to the side and/or bottom surfaces of the reaction vessel as a porous solid product during the production.

Another method known in the art is one in which a reaction takes place between titanium tetrachloride and magnesium on the surface of a titanium ribbon to produce titanium by depositing it on the surface. This is disclosed in Japanese Patent Publication No.3004/1958. Unfortunately, this method causes the metal product to deposit on the ribbon and also on a frame supporting the ribbon.

Accordingly, the prior art fails to provide a continuous operation for producing titanium because of the necessity to remove the deposited metal prior to carrying out subsequent steps. For this reason, the prior art methods are compelled to employ a batch process which causes discontinuity and inefficiency in the manufacturing operation. Furthermore, solid titanium or the like deposited to the inner surface of the reaction vessel is readily contaminated by the material of the reaction vessel since it is highly reactive at the elevated process temperatures, to a degree sufficient to react the reactants, resulting in deterioration in the quality and purity of the metal product.

It is therefore an object of the present invention to provide a method for the production of a metal from its metal halide which is capable of continuously producing homogeneous metal of high quality by reduction of the metal halide.

According to the present invention, there is provided a method for producing a metal by the reduction of its metal halide using a reducing metal agent, characterized by the steps of: charging a reaction vessel with particles of the same metal as the metal product; injecting a gas upwards into the reaction vessel from its lower portion to cause the metal particles in the reaction vessel to form a fluidized bed of the metal particles; introducing the metal halide and reducing metal agent into the reaction vessel; and causing a reducing reaction of the metal halide with the reducing metal agent on the surface of the metal particles at a temperature below the melting point of the metal product and at

a pressure below a vapour pressure of each of the reducing metal agent and the metal halide at the reaction temperature.

The metal particles serve as reaction nuclei. This then results in depositing and growing the metal product on the surface of the metal particles. The metal particles on which the metal product is deposited can be continuously tapped out from the reaction vessel.

The injected gas may comprise the metal halide and the reducing metal agent and is injected in vapour form from the lower portion of the reaction vessel to cause the metal particles to fluidize, in order to form the fluidized bed of the metal particles. Alternatively, the reducing metal agent may be fed in liquid form to a reaction zone in the reaction vessel while the injected gas comprises the metal halide injected upwards in vapour form from the lower portion of the reaction vessel to cause the metal particles to fluidize, in order to form the fluidized bed of the metal particles. Alternatively, the injected gas may be an inert gas injected upwards from the lower portion of the reaction vessel to cause the metal particles to fluidize in order to form the fluidized bed of the metal particles.

The metal halide may be titanium chloride, zirconium chloride, silicon chloride, tantalum chloride or niobium chloride. The reducing agent may be magnesium or sodium.

When the metal halide is titanium tetrachloride and the reducing agent is magnesium, the reaction may be carried out at a temperature in the range of 1000°C to 1200°C, preferably at about 1100°C. The reaction may be carried out at a pressure in the range of 20 to 50 Torr; preferably 50 Torr.

The invention may be carried into practice in various ways and some embodiments will now be described by way of example with reference to the accompanying drawings in which the single figure is a block diagram showing a system for practicing a method according to the present invention.

The following embodiment comprises the reduction of titanium tetrachloride to metal titanium using magnesium as a reducing agent.

As shown in the Figure, titanium tetrachloride feedstock is supplied at a predetermined rate from a storage tank 1 by means of a metering pump 2 to an evaporator 3. The titanium tetrachloride is heated to vaporize and then superheated in the evaporator 3.

Molten magnesium as a reducing agent is fed from a storage vessel 4 to a magnesium purifier 45 where it is passed through a filter, such as a titanium sponge layer so that impurities, such as

iron, chromium, nickel and the like and also oxygen, nitrogen and the like remaining in the magnesium may be satisfactorily removed. The purified molten magnesium is then fed to a magnesium evaporator 7 by means of a pump 6 and heated to vaporize.

During these operations, the titanium tetrachloride evaporator 3 and the magnesium evaporator 7 may be kept substantially at an atmospheric pressure.

The titanium tetrachloride and magnesium vapours are then supplied at a predetermined rate through pipes 8 and 9 to a reaction vessel 10 and ejected from the bottom of the reactor vessel 10 through separate injection pipes 8 and 9 into the reaction vessel 10.

The reaction vessel 10 is also supplied with a predetermined amount of titanium particles, which are to act as reaction nuclei from a hopper 11 located above the reaction vessel 10. The titanium particles are selected from commercially available titanium powders, fine titanium particles obtained from the production of titanium sponge, titanium chips produced from cutting titanium ingot and then further powdered.

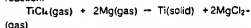
The reaction vessel 10 is kept at a temperature below the melting point of the metal to be produced, and is evacuated to a lower pressure which prevents magnesium and magnesium chloride from being condensed at the temperature. The temperature in the reaction vessel 10 is preferably kept as low as possible to facilitate the selection of a material for the reaction vessel. However, the inner surface of the reaction vessel 10 is desirably kept at a temperature as high as possible and at a pressure as low as possible for the purpose of preventing magnesium and magnesium chloride from condensing on the inner surface. Also, in order to discharge magnesium chloride as a by-product of the reaction in the reaction vessel 10 and excess magnesium from the reaction system to recover them in liquid form in a condenser 15, the condenser 15 is preferably maintained at a higher pressure. In order to meet these contradictory requirements, the process of the present invention may be practiced under conditions where the temperature and pressure in the reaction vessel 10 are set at about 1100° C and about 50 Torr, respectively.

The titanium tetrachloride and magnesium vapours supplied to the reaction vessel 10 are ejected upwards from the lower portion thereof because the reaction vessel 10 is maintained at a lower pressure, so that the energy imparted by the vapours due to their injection causes the titanium particles charged in the reaction vessel 10 to fluidize in the reaction vessel 10.

This fluidization of the titanium particles in the

reaction vessel 10 may also be carried out by upwardly ejecting an inert gas such as argon from the lower portion of the reaction vessel 10 rather than using the energy imparted by the titanium tetrachloride and magnesium vapours, to form a fluidized bed of the titanium particles in the reaction vessel. In this case, the titanium tetrachloride and magnesium vapours may be ejected into the fluidized bed of the titanium particles, and then the magnesium somewhat in excess as compared to the stoichiometric amount may be supplied to the reaction vessel 10 in order to complete the reaction of the titanium tetrachloride and magnesium.

Injection of the titanium tetrachloride and magnesium vapours into the fluidized bed of the titanium particles in the reaction vessel 10 causes the intensive exothermic reaction between the two vapours. As a result, the magnesium reduces the titanium tetrachloride on the surface of the titanium particles which form the fluidized bed and which serve as reaction nuclei, according to the following reaction:



The titanium thus produced due to the reaction on the surface of the titanium particles deposited on the surface of the titanium particles, so that the titanium particles gradually increase in diameter and weight in the fluidized state in the reaction vessel 10.

The temperature of the reaction zone in the reaction vessel is kept below the melting point of the metal product, and its pressure is kept below the vapour pressure of both magnesium and magnesium chloride at that temperature. This causes the titanium tetrachloride and magnesium to react in the vapour phase to produce the titanium depositing on the surface of the titanium particles while it is growing. At the same time, the magnesium chloride, as a by-product of the reaction, and the unreacted magnesium are discharged in a mixed gas from the reaction system without condensing in the reaction zone.

Carrying out the present invention under conditions in which the reaction zone is set at a temperature of 1100° C and a pressure of 50 Torr causes the magnesium to be maintained in the vapour state in the reaction zone, since the vapour pressures of magnesium chloride and magnesium at this temperature are 86 Torr and 736 Torr, respectively. They are therefore discharged from the reaction zone without condensing to a subsequent cooling zone in which they are liquified or solidified for recovery.

The reducing reaction develops on the surface of the titanium particles to which the reaction product deposits, and promotes successive deposition and growth of the titanium. When the diameter of

the titanium particles has increased to from twice to four times their initial diameter, the titanium particles are drawn out from the fluidized bed in the reaction vessel 10 continuously through a tapping port 12 to a cooler 13, in which the particles are water-cooled to a room temperature. The cooled titanium particles are removed via a valve, such as, for example, a rocker valve and charged to a screen classifier 14, which classifies the metal particles into a fine particle group with a diameter of 0.5mm or less and a coarse particle group with a greater diameter. The coarse particle group is the product and the fine particle group is returned to the reaction vessel 10 via the hopper 11 for use as reaction nuclei.

The vapour mixture of magnesium chloride by-product and excess magnesium discharged from the reaction vessel 10 is directed to a condenser 15 where it is condensed to a liquid. The liquified magnesium chloride and magnesium are then collected through a "vacuum leg" into a liquid separator 16, that are separated from each other due to the difference in their densities. The separated magnesium is returned to the reaction vessel 10 for reaction and separated magnesium chloride is recovered and fed to electrolytic cells (not shown).

In the Figure, reference numeral 17 designates a vacuum pump for reducing the pressure in the apparatus.

In a reaction system constructed as described above, vapours of titanium tetrachloride and magnesium are ejected into a reaction vessel maintained at a reduced pressure, and form a fluidized bed therein, so that the reducing reaction between them takes place on the surface of the titanium particles which act as nuclei for producing titanium. Accordingly, the titanium deposits and grows on the surface of the titanium particles without depositing on the wall of the reaction vessel, which is free from any contamination by the material of the wall of the reaction vessel. Also, in the present invention, the titanium particles which are used as reaction nuclei inherently have a larger specific surface area. This results in a significant increase in the efficiency of the reaction. Furthermore, in the present invention, the reaction zone is kept at a lower pressure. Accordingly, excess magnesium and any magnesium chloride by-product which might otherwise remain in fine internal voids of the titanium particles are subjected to vacuum distillation while the titanium particles are fluidized in the reaction vessel, resulting in the production of metal particles of high purity which are substantially free from magnesium and magnesium chloride.

The above process has been described in connection with the production of metal titanium, however, it is to be understood that the present inven-

tion is also applicable to the production or manufacture of zirconium, silicon, tantalum, niobium and the like. Also, in the present invention, sodium may be used as a reducing metal agent.

The present invention will now be illustrated with reference to the following non-limiting examples.

#### Example 1

A reaction vessel of 20cm inner diameter and lined with titanium was charged with 12kg of titanium particles have a diameter of about 0.2 to 2mm, a surface area of about  $12.6 \times 10^{-4}$  to  $12.8 \times 10^{-4} \text{ m}^2$  and a weight of about  $18.8 \times 10^{-3}$  to  $18.8 \times 10^{-4} \text{ kg}$ . The reaction vessel was subjected to external heating and kept at a temperature of  $1100^\circ \text{C}$  while the pressure in the reaction vessel was reduced to 50 Torr by a vacuum pump.

Titanium tetrachloride vapour superheated to  $372^\circ \text{C}$  and magnesium vapour heated to  $1120^\circ \text{C}$  were separately ejected from individual injection ports to the lower portion of the reaction vessel at feed rates of 7980g/hr and 2539.2g/hr, respectively, so as to fluidize the titanium particles in the reaction vessel.

Injection of the titanium tetrachloride and magnesium into the reaction vessel in this way resulted in a simultaneous reaction, which in turn resulted in the temperature in the reaction vessel tending to rise. In order to maintain the reaction vessel at a desirable temperature, the external heating was controlled to keep the temperature at  $1100^\circ \text{C}$ .

After the reaction had been taking place for one hour, metal particles of 2012g were drawn out from a tapping port. A residue of magnesium added in excess amount of 20% and magnesium chloride were cooled in a condenser and then separated by a liquid separator. As a result, magnesium chloride of 8455.8g was recovered in liquid form.

The metal particles thus produced were formed of titanium deposited and grown on the surface of the titanium particles serving as reaction nuclei, and were substantially free from contamination by the material of the reaction vessel wall. Also, no magnesium chloride nor any of the excess magnesium remained in the fine internal voids of the metal particles. Thus, the metal product was very pure.

#### Example 2

A reaction vessel of 30cm inner diameter and lined with titanium was charged with 30kg of titanium particles used in the Example 1. The reac-

tion vessel was heated by an external heater and kept at a temperature of 1100°C while the pressure in the reaction vessel was reduced to 50 Torr by means of an automatic pressure controller.

Titanium tetrachloride and magnesium vapours were separately ejected from individual injection ports to the lower portion of the reaction vessel at feed rates of 17.95kg/hr and 5.7kg/hr, respectively, so as to fluidize the titanium particles in the reaction vessel.

Injection of the titanium tetrachloride and magnesium into the reaction vessel in this way resulted in a simultaneous reaction, which in turn resulted in the temperature in the reaction vessel tending to rise. In order to maintain the reaction vessel at a desirable temperature, the external heating was controlled to keep the temperature at 1100°C.

After ten minutes, metal particles were started to be drawn out from a tapping port at a rate of 5.43kg/hr. After cooling, the metal particles thus produced were subjected to screening, and particles of 0.5mm or below were returned to the fluidized bed from the top of the reaction vessel at a rate of 0.9kg/hr.

A magnesium chloride by-product and an excess magnesium, the total amount of which was 19.0kg/hr, were condensed in a condenser maintained at 777°C and obtained in liquid form through a vacuum leg.

The reaction was continued for five hours. The metal particles thus produced were formed of titanium deposited and grown on the surface of the titanium particles serving as reaction nuclei, and were substantially free from contamination by the material of the reaction vessel wall. Also, no magnesium chloride nor any of the excess magnesium remained in the fine internal voids of the metal particles. Thus, the metal product was very pure.

### Example 3

Example 1 was repeated except that the titanium tetrachloride and magnesium were injected into a reaction vessel in the form of gas and liquid and at feed rates of 8kg/hr and 2.6kg/hr, respectively.

The reaction proceeded in substantially the same manner as in Example 1. After two hours, the reaction was terminated and titanium particles of about 4.0kg were recovered from the reaction vessel. The particles had a particle size of 0.3 - 2.2mm and an average particle diameter of 0.8mm.

### Comparative Example 1

A vapour phase reaction between titanium tetrachloride and magnesium was conducted under substantially the same conditions as Example 1 except that titanium particles were not charged into a reaction vessel initially.

It was observed that a small amount of titanium was produced on the wall of the reaction vessel. However, most of the product was discharged to a condenser in the form of lower chlorides of titanium without forming any metal titanium.

### Claims

1. A method for producing a metal by the reduction of its metal halide using a reducing metal agent, characterized by the steps of: charging a reaction vessel with particles of the same metal as the metal product; injecting a gas upwards into the reaction vessel from its lower portion to cause the metal particles in the reaction vessel to form a fluidized bed of the metal particles; introducing the metal halide and reducing metal agent into the reaction vessel; and causing a reducing reaction of the metal halide with the reducing metal agent on the surface of the metal particles at a temperature below the melting point of the metal product and at a pressure below a vapour pressure of each of the reducing metal agent and the metal halide at the reaction temperature.

2. A method as claimed in Claim 1 characterized by continuously tapping the metal product deposited on the metal particles from the reaction vessel.

3. A method as claimed in Claim 1 or Claim 2, characterized in that the injected gas comprises the metal halide and the reducing metal agent and is injected in vapour form from the lower portion of the reaction vessel to cause the metal particles to fluidize, in order to form the fluidized bed of the metal particles.

4. A method as claimed in Claim 1 or Claim 2 characterized in that the reducing metal agent is fed in liquid form to a reaction zone in the reaction vessel while the injected gas comprises the metal halide injected upwards in vapour form from the lower portion of the reaction vessel to cause the metal particles to fluidize, in order to form the fluidized bed of the metal particles.

5. A method as claimed in Claim 1 or Claim 2 characterized in that the injected gas is an inert gas injected upwards from the lower portion of the reaction vessel to cause the metal particles to fluidize in order to form the fluidized bed of the metal particles.

5. A method as claimed in any preceding claim characterized in that the metal halide is titanium chloride, zirconium chloride, silicon chloride, tantalum chloride or niobium chloride.

7. A method as claimed in any preceding claim characterized in that the reducing metal agent is magnesium or sodium.

8. A method as claimed in any preceding claim characterized in that the reaction is carried out at a temperature of 1100 °C and a pressure of 20 - 50 Torr.

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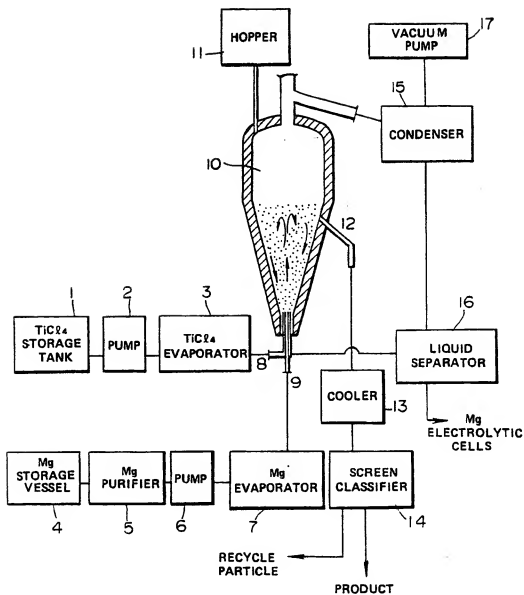
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European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number

EP 88 30 6110

## DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	US-A-3 012 862 (L. BERTRAND et al.) * claim 1 *	1	C 22 B 5/04 C 22 B 34/12
A	US-A-2 827 371 (J.P. QUIN) * claims 6,9 *	1	
A	US-A-2 997 385 (C.H. WINTER, JR.) * claim 1 *	1	
A	GB-A- 736 852 (THE NATIONAL SMELTING CO.) ----		
A	CHEMICAL ABSTRACTS, vol. 53, 10th January - 25th February 1959, page 12145f, abstract no. 12145f, Columbus, Ohio, US; S. TAKEUCHI et al.: "Apparatus for continuous production of pure titanium and zirconium", & JP - B - 58 3004 (Cat. D) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 22 B 5/04 C 22 B 34/12
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 26-08-1988	Examiner SUTOR W
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technical-gical background O : non-written disclosure P : intermediate document			

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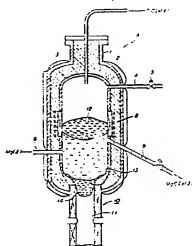
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Method for producing metallic titanium and apparatus therefor.

A method for producing metallic titanium (34) by the reduction of titanium tetrachloride with a reducing metal agent, capable of continuously producing metallic titanium on an industrial scale. The temperature and pressure of the reaction zone (12) are kept above the melting point of metallic titanium and at least above the vapour pressure of the reducing metal agent, respectively, so that the reducing metal agent and its chloride (13) may be kept in a molten state but without boiling.

FIG. 1



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23, 23, 26, 30, 31, 35, 36, 38, 43, 44, 51

43-49, 51-103

50- w/Na

## Description

## METHOD FOR PRODUCING METALLIC TITANIUM AND APPARATUS THEREFOR

This invention relates to a method for producing metallic titanium and an apparatus therefor, and more particularly to a method and apparatus for producing metallic titanium from titanium tetrachloride at a reaction temperature above the melting point of titanium.

In the known "Kroll" method, metallic titanium is produced by the reduction of titanium tetrachloride by metallic magnesium.

In the Kroll method, the reduction reaction is generally carried out at a temperature below the melting point of metallic titanium while keeping the reduction vessel at normal or reduced pressure to produce spongy metallic titanium. The spongy metallic titanium product is subjected to vacuum separation or leaching to remove any excess metallic magnesium and magnesium chloride (by-product) remaining in the fine internal voids of the metallic titanium product and is thus purified. The purified metallic titanium is then crushed and formed into a shape suitable for melting. After melting, an ingot of titanium is formed.

As can be seen, the Kroll method is a batch type process. Accordingly, producing the metallic titanium ingot according to the Kroll method requires at least four discontinuous or independent steps comprising a reduction reaction step, a vacuum separation step, a crushing step and a melting step.

The Kroll method also has the following disadvantages.

The spongy metallic titanium which is the reaction product is firmly adhered to a reduction reaction vessel, so that much labour and time are required for peeling the adhered reaction product from the vessel.

Another disadvantage is that it is very difficult to remove the heat of reaction from the reaction system during the reduction step sufficiently rapidly.

A further disadvantage is that the titanium is produced at a sufficiently elevated temperature to increase its activity. Accordingly, it is readily polluted with the material of the reaction vessel wall.

Still another disadvantage is that the separation step for purification of the titanium requires much attention in order to prevent contamination of the titanium with moisture, air and the like. Accordingly, removal of the unreacted material and the by-product must be carried out in a vacuum or argon atmosphere.

For the purpose of reducing metal halide with a reducing metal agent without using the Kroll method other methods are proposed in each of which the reduction reaction is carried out at a reaction temperature above the melting point of the metal to be produced and the product is continuously removed from the reaction vessel. The metal product is then obtained in a molten state or in the form of an ingot by cooling the molten metal product for solidification.

As an example, Japanese Patent Application Laying-Open Publication No.35733/1981 discloses a method for producing metallic titanium which comprises the steps of introducing titanium chloride and a reducing metal agent both in the vapour state into a reaction vessel to react both under conditions so that a liquid metallic titanium product is obtained together with the chloride of the reducing metal agent in the form of a vapour. The chloride by-product of the reducing metal agent is separated from the titanium product for recovery and the metallic titanium product is solidified in a mould kept at a temperature below the melting point of the metallic titanium product to obtain an ingot which is removed from the reaction vessel.

Japanese Patent Publication No.19761/1971 discloses a method for producing metal comprising the steps of introducing titanium tetrachloride vapour and a liquid reducing metal agent into liquid metal in a reaction vessel, heating a reaction zone to a temperature above the melting point of titanium to obtain a metallic titanium product and a chloride by-product of the reducing metal agent in a molten state under a vapour pressure of the reducing metal agent at the relevant temperature, separating the product and by-product from each other using the difference in their gravities, and separately removing them from the reaction vessel.

Various similar methods have attempted to solve the problems of the Kroll method by reducing the metal halide with the reducing metal agent while keeping the reaction temperature above the melting point of the metal product to obtain the molten metallic titanium product. However, while these methods are disclosed in the patent literatures, they have not been commercialised on an industrial scale. The reason is believed to be that it is very difficult to select a material for the reaction vessel which withstands a sufficiently high temperature to produce active metal of a high melting point such as titanium, zirconium or the like in the reaction vessel and to keep it in a molten state.

More particularly, for example, the method taught in Japanese Patent Publication No.19761/1971 is to reduce titanium tetrachloride with magnesium to produce metallic titanium while keeping the temperature in the reaction zone at about 1730°C and the pressure in the reaction vessel at about 5 atms corresponding to a partial pressure of the magnesium chloride by-product at that temperature to produce the metallic titanium product and the magnesium chloride by-product in a molten state. Thus, in the method the reaction zone temperature is about 1720°C and its pressure is about 5 atms which is substantially equal to the vapour pressure of the magnesium chloride, produced in liquid form. This results in the magnesium boiling which leads to a failure to maintain the magnesium in an amount sufficient to reduce titanium tetrachloride in the reaction zone fully. This causes the reaction to take place in the presence of insufficient magnesium which often produces lower chlorides of titanium such as titanium trichloride, titanium dichloride and the like.

Also, in this method, the reactants (titanium tetrachloride in the form of a gas and magnesium in the form of a liquid) are supplied through graphite pipes to a molten layer of the reaction product the bottom of the

reaction vessel to carry out the reaction in the molten layer. This causes the open end of the graphite pipes to be corroded by the active molten titanium product. Also, the molten titanium product contacts each of the reactants at a relatively low temperature at the open end of the pipes, solidifying the reactants, and so clogging the pipes. Furthermore, since the reaction is a reduction reaction taking place in the molten layer of titanium, the titanium product is contaminated with unreacted reactants, the by-product and the like. Moreover, the lack of magnesium in the reaction zone leads to a decrease in reaction efficiency per a reaction sectional area.

It is an object of the present invention to provide a method and apparatus for producing metallic titanium by the reduction of titanium tetrachloride by a reducing metal agent which are capable of continuously producing metallic titanium at a lower energy cost and on an industrial scale.

According to one aspect of the invention, there is provided a method for producing a metal (e.g. titanium) by the reduction of the product metal (e.g. titanium) tetrachloride with a reducing metal agent characterised by the steps of: maintaining the temperature and pressure in a reaction zone in a reaction vessel above the melting point of the product metal (e.g. metallic titanium) to be produced and above the vapour pressure of the reducing metal agent at that temperature; supplying the product metal (e.g. titanium) tetrachloride and the reducing metal agent to the reaction vessel to react to produce the product metal (e.g. a metallic titanium) and a chloride by-product of the reducing metal agent while maintaining the product and the by-product in a molten state; separating the product metal (e.g. metallic titanium) and the chloride by-product of the reducing metal agent from each by making use of the differences in their densities; collecting the product metal (e.g. metallic titanium) at the bottom of the reaction vessel; and continuously drawing out the product metal (e.g. metallic titanium) from the bottom of the reaction vessel.

Preferably, the titanium product is solidified by cooling as it is withdrawn.

Preferably, a molten bath of chloride of the reducing metal agent and optionally also of the reducing metal agent itself is previously formed in the reaction vessel so that the surface of the molten bath constitutes the reaction zone and titanium tetrachloride and the reducing metal agent are supplied to the reaction zone. Preferably the titanium tetrachloride is supplied in liquid form from the top of the reaction vessel and the reducing metal agent is supplied either in the same way or is injected into the bath.

Preferably, the chloride by-product of the reducing metal agent is discharged from the reaction vessel at a rate arranged to maintain the position of the reaction zone substantially constant. The method may also include the steps of inserting a titanium ingot into the bottom of the reaction vessel resulting in the coalescence of the separated metallic titanium metal product with the titanium ingot and drawing the metallic titanium product out continuously together with the titanium ingot at a rate corresponding to the amount of the metallic titanium product being coalesced with the titanium ingot.

According to another aspect of the invention, there is provided an apparatus for producing metallic titanium by the reduction of titanium tetrachloride with a reducing metal agent characterised by: a reaction vessel having a reaction zone in which a temperature above the melting point of the titanium product is defined and which is kept at a pressure sufficient to prevent boiling of the reducing metal agent and its chloride at that temperature; a reducing metal agent feed pipe for supplying the reducing metal agent in the form of a liquid from the side or the top of the reaction vessel to the reaction zone; a titanium tetrachloride feed pipe for supplying titanium tetrachloride from the top of the reaction vessel to the reaction zone; a discharge pipe for discharging the chloride by-product of the reducing metal agent from the side of the reaction vessel; heating means arranged outside the reaction vessel at a position corresponding to the reaction zone and a withdrawing section at the bottom of the reaction vessel for continuously drawing out the metallic titanium product.

One preferred embodiment of the invention includes a reaction vessel made of thick titanium plate in which a reaction zone is defined and which is kept at a pressure sufficient to prevent boiling of the reducing metal agent and its chloride. A reducing metal agent feed pipe supplies the reducing metal agent in the form of a liquid from the side or top of the reaction vessel to the reaction zone, and a titanium tetrachloride feed pipe supplies titanium tetrachloride from the top of the reaction vessel to the reaction zone. A discharge pipe for discharging a chloride by-product of the reducing metal agent extends from the side of the reaction vessel. Heating means are arranged outside the reaction vessel at a position corresponding to the reaction zone for carrying out electromagnetic induction heating, resistance heating or the like, and a mould section is arranged at the bottom of the reaction vessel for solidifying the molten metallic titanium product by cooling and continuously drawing out it from the reaction vessel.

An alternative reaction vessel structure includes a reaction vessel made of metal such as copper or a ceramic material such as alumina, zirconia or the like in which a reaction zone is defined and which is kept at a pressure sufficient to prevent boiling of the reducing metal agent material and its chloride. The reaction vessel has a vertically extending hollow shape and is open at the top and bottom. The reaction vessel includes a cooling agent circulating path for cooling the inner surface of the reaction vessel and portions of its outer periphery at a position corresponding to the reaction zone. The vessel also includes a removal section with heating means for heating a molten material which carries out electromagnetic induction heating, resistance heating or the like.

In the present invention, a suitable reaction vessel provided with the heating means may comprise a crucible, as disclosed in U.S. Patent No. 3,755,091 which is adapted to melt titanium chips, titanium sponge or the like for preparing a titanium ingot and is used in an evacuated inert atmosphere. Such a crucible may be incorporated in a pressure vessel for use as the reaction vessel in the present invention which includes the

reaction zone for reducing titanium tetrachloride and the mould section for solidifying the metallic titanium product by cooling and continuously removing it therefrom.

The present inventors have conducted the following reaction test in order to evaluate the reaction efficiency for reducing titanium tetrachloride with metallic magnesium according to the present invention.

#### REACTION TEST

A pressure in the reaction vessel was kept at 50 atms. The reaction vessel was charged with 845g metallic magnesium, which was heated to 1350°C by electromagnetic induction heating or resistance heating to form a molten magnesium bath in the reaction vessel. Immediately after the heating, 1340g liquid titanium tetrachloride was fed to the molten magnesium for 50 seconds at a feed rate of 1608g/min.

The temperature of the bath reached the melting point of titanium in 15 seconds after the beginning of the addition of titanium tetrachloride, thereby producing liquid titanium. The yield of titanium was 99% and the reaction efficiency per unit sectional area of the reaction vessel was 62.7 kmol/hr m<sup>2</sup>. For comparison, the Kroll method was carried out and was found to give a reaction efficiency per unit sectional area of a reaction vessel of 1.3 kmol/hr m<sup>2</sup>.

The efficiency of reaction between titanium tetrachloride and metallic magnesium in the gas phase is calculated in an article entitled "Gas Phase Reaction Test Report" by Professor Takeuchi of Tohoku University, Journal of Japan Institute of Metals, 23, pp625-637 (1965), as follows:

In the reaction test, the volume of a titanium ribbon for growing titanium on was 0.057 m<sup>3</sup> and the deposition rate of titanium on to the titanium ribbon was 3.45kg/hr (72mol/hr). Accordingly, its volume efficiency is 72/0.057 = 1263mol/hr m<sup>3</sup> and its reaction efficiency per area is 1.263kmol/hr m<sup>2</sup>.

It may not be strictly fair simply to compare the reaction efficiency of the present invention to the reaction efficiency calculated in this way because reaction conditions such as temperature, a feed rate of feedstocks and the like were set differently. However, it will be noted that the reaction between the titanium tetrachloride and metallic magnesium in the present invention exhibits a reaction efficiency at least 49.6 (62.7/1.263) times that of the above described gas phase reaction and 48.2 (62.7/1.3) times as much as that of the Kroll process. The fact that the present invention exhibits such a higher reaction efficiency is believed to be due to the liquid metallic magnesium and liquid titanium tetrachloride being supplied to the reaction zone kept there at a high temperature and a high pressure.

The temperature of the reaction zone is set above the melting point of titanium. In order to precipitate stably the metallic titanium product onto the bottom of the reaction vessel while keeping it in a molten state, it is desirable to keep the reaction vessel at a temperature which is about 100-200°C higher than the melting point of titanium and to keep the pressure of the reaction zone at least above the vapour pressure of the reducing metal agent at the reaction temperature and preferably above the sum of the vapour pressures of the reducing metal agent and its chloride.

More preferably, when titanium (melting point of 1670°C) is to be produced using titanium tetrachloride as the feedstock and magnesium as the reducing metal agent, the bath in the reaction vessel is kept at a temperature of at least 1670°C and more preferably 1827°C, and at a pressure above 42.6 atms, corresponding to the partial pressure of magnesium and more preferably above 48.6 atms corresponding to the total sum of the partial pressure of magnesium (42.6

For reduction of titanium tetrachloride, the reducing metal agent may be used in a stoichiometric amount. However, in order to carry out the reduction fully, it is desirable to use a predetermined excess of the reducing metal agent in the reaction zone to inhibit the production of lower titanium chlorides.

The invention may be carried into practice in various ways and some embodiments will now be described by way of example with reference to the accompanying drawings, in which:

Figure 1 is a vertical section through a first embodiment according to the present invention;

Figure 2 is a view similar to Figure 1 showing a second embodiment; and

Figure 3 is a partially cutaway perspective view generally showing an example of a reaction vessel incorporated in the apparatus shown in Figure 2.

In the present invention, titanium tetrachloride and a reducing metal agent are supplied in liquid form to a reaction zone for reaction. Magnesium or sodium may be used as the reducing metal agent.

The apparatus shown in Figure 1 includes a reaction vessel structure A which also serves as a pressure vessel. The reaction vessel structure A includes an outer shell or outer wall 1 made of a steel plate, an inner wall made of titanium serving as a reaction vessel 3 and a heat insulating material 2 between the outer shell 1 and the reaction vessel 3.

An inert gas (e.g. argon) is introduced to the reaction vessel 3 from a pressure adjusting pipe 4 through a valve 5, so that the interior of the reaction vessel 3 is set and kept at a pressure sufficient to prevent substantially any boiling of the magnesium and vessel 3 is set and kept at a pressure sufficient to prevent substantially any boiling of the magnesium and magnesium chloride, even when the temperature in a reaction zone defined in the reaction vessel 3 rises above the melting point of titanium. For example, the reaction vessel 3 is kept at a pressure of about 50 atms when the temperature of the bath in the reaction vessel 3 is 1827°C. When the pressure in the reaction vessel 3 is above or below the set value, an automatic pressure adjusting valve (not shown) is operated to keep the pressure at the set value automatically.

Liquid magnesium for use as the reducing metal agent is supplied to the reaction zone through a reducing

metal agent feed pipe 6 extending through the side wall of the reaction vessel structure A and into the reaction vessel 3. Similarly, liquid titanium tetrachloride is supplied to the reaction zone through a titanium tetrachloride feed pipe 7 extending through the top of the reaction vessel structure A and into the vessel 3.

The reaction vessel 3 is provided at an intermediate part of its outer periphery (in a vertical direction) surrounding the reaction zone with a heater or heating means 8 adapted to carry out electromagnetic induction heating, resistance heating or the like to adjust the temperature of the reaction zone in the reaction vessel 3 to a level above 1670°C, corresponding to the melting point of titanium. A discharge tube 9 is connected to the reaction vessel 3 adjacent to the heating means 8, for discharging magnesium chloride by-product formed by the reduction reaction.

A mould section 10 for solidifying the molten metallic titanium product is connected at the bottom of the reaction vessel, for cooling and drawing out the titanium product.

The production of metallic titanium using the apparatus shown in Figure 1 will now be described.

Firstly, a titanium ingot 11 is inserted in the mould section 10 to close the bottom of the reaction vessel 3 and then magnesium and magnesium chloride are charged in small amounts into the reaction vessel 3. The atmosphere in the reaction vessel 3 is replaced with argon gas and then the heater 8 is operated to melt the magnesium and magnesium chloride, resulting in a molten bath of magnesium and magnesium chloride being formed in the reaction vessel 3. The molten magnesium 12 floats above the magnesium chloride due to the difference in their densities, so that it may remain separate from the magnesium chloride.

Subsequently, more argon gas is introduced into the reaction vessel 3 to increase the pressure. Then, liquid titanium tetrachloride is fed to the surface of the molten magnesium 12 through the titanium tetrachloride feed pipe 7 connected to the top of the reaction vessel 3. Liquid magnesium is supplied to the molten magnesium chloride through the magnesium feed pipe 6 connected to the side of the reaction vessel 3. Alternatively, the magnesium feed pipe 6 may be connected to the top of the reaction vessel 3 so that both the titanium tetrachloride and the magnesium may be supplied in liquid form from the top of the reaction vessel 3 to the reaction zone (as in the apparatus of Figure 2 described hereinafter).

Titanium tetrachloride supplied to the surface of the molten magnesium layer of the bath reacts as a liquid with the liquid magnesium to produce titanium 14 and magnesium chloride 13. Alternatively, it may react as a vapour with magnesium vapour vapourised from the molten magnesium phase of the bath or indeed with liquid magnesium.

The heat of reaction and the effect of the heater 8 cause the temperature of the molten bath in the reaction vessel 3 to rise above the melting point of titanium. However, the reaction vessel 3 is kept at a pressure above the vapour pressure of magnesium at that temperature, so the titanium product 14, the magnesium chloride by-product 13 and the magnesium 12 are all kept in a liquid state. Also, the molten bath is vertically separated into three layers, namely magnesium 12, magnesium chloride 13 and titanium 14, in that order, due to the differences in their densities.

The molten metallic titanium product 14 precipitates and sinks through the molten magnesium layer and the molten magnesium chloride layer to the bottom of the reaction vessel 3 and reaches the top of the titanium ingot 11 to coalesce with it as it is produced. Correspondingly, the titanium ingot 11 is continuously drawn out at a suitable rate, during which the titanium is solidified by cooling.

The magnesium chloride by-product 13 is discharged through the discharge pipe 9 connected to the side of the reaction vessel 3 at a discharge rate which is adjusted so that the molten bath in the reaction zone is kept constant in depth. The titanium ingot 11 is drawn out at a rate corresponding to the amount of titanium precipitated on the titanium ingot (or the precipitation rate of the titanium) by means of rollers (not shown). Accordingly, the position of the molten titanium product above the titanium ingot 11 is kept substantially constant.

The apparatus shown in Figures 2 and 3 is constructed in substantially the same manner as that of Figure 1 except for the construction of the reaction vessel 3, the arrangement of the reducing material feed pipe 6 and the construction of the heater or heating means 8.

More particularly, the reaction vessel 3 is formed as a vertically extending cylindrical shape, the top and bottom of which are open and is divided into two or more segments 32 by means of vertical slits 31 in the wall of the reaction vessel 3. In the illustrated embodiment, it is divided into twelve segments 32. Each of the segments 32 is formed of a material of good thermal conductivity for example, a metal such as copper or the like. The slits 31 are filled with an electrically insulating and heat resistant material to insulate the segments 32 from one another electrically. The segments 32 are each provided with an internal cooling pipe 33 for supplying a cooling agent through them to cool the wall of the reaction vessel 3 defining the reaction zone therein. The cooling pipes 33 are connected to one another and between a cooling agent inlet 34 and a cooling agent outlet 35 to form a path for circulating a cooling agent.

An upwardly extending duct 15 is connected to the open top end of the reaction vessel, the upper end of which is connected to the exterior through a cylinder section 16 and in which the reducing agent feed pipe 6 is located. The titanium tetrachloride feed pipe 7 is positioned within the upper portion of the reaction duct 15. Thus, liquid magnesium and liquid titanium tetrachloride are supplied through the feed pipes 6 and 7 to the reaction zone. The reaction vessel 3 is provided at a bottom thereof with a mould section 19, through which a titanium ingot 11 is inserted into the reaction vessel 3.

The reaction vessel 3 constituted by the segments 32 has at its upper part on the outer periphery at a position corresponding to the reaction zone in the reaction vessel 3, an upper electromagnetic induction

heating coil 8a for raising a temperature of the reaction zone above the melting point of titanium (or 1670°C). On its lower part, the vessel 3 has a lower electromagnetic induction heating coil 8b for melting the top of the titanium ingot 11 and the magnesium chloride adjacent the top to keep the top of the ingot constantly in a molten state during the reaction. Thus, in the illustrated embodiment, the heating means 8 comprises the upper and lower electromagnetic induction heating coils 8a and 8b.

As described above, the embodiment of Figures 2 and 3 is so constructed that the reaction vessel 3 is divided into a plurality of the cooled segments 32 and the segments 32 are electrically insulated from one another by the slits 31. Such a construction substantially prevents the generation of eddy currents in each segment 32 due to electromagnetic induction heating, thereby permitting the molten materials in the reaction zone of the reaction vessel 3 and the top of the titanium ingot to be subjected to induction heating without heating the segments 32. The apparatus includes a discharge pipe 9 for discharging the magnesium chloride by-product which is connected to a substantially central portion of a side of the reaction vessel, in this case between the upper and lower heating coils 8a and 8b.

In the illustrated embodiment, the reaction vessel 3 is made of a metal agent in view of economic efficiency and maintenance. However, it may be formed of a ceramic material such as alumina, zirconia or the like. In such a case, it would not be necessary to divide the reaction vessel 3 into segments.

The operation of the apparatus shown in Figures 2 and 3 will now be described. Basically, operation of the apparatus of Figures 2 and 3 is similar to that of Figure 1.

First, a titanium ingot 11 is inserted into the mould section 10 to close the bottom of the reaction vessel 3 and then magnesium and magnesium chloride are charged in small amounts into the reaction vessel 3. Then, the atmosphere in the reaction vessel 3 is replaced with argon gas and the lower magnetic induction heating coil 8b is operated to melt the top of the titanium ingot 11 while the upper magnetic induction heating coil 8a is operated to melt the magnesium and magnesium chloride charged into the reaction zone, resulting in a molten bath of magnesium and magnesium chloride being formed in the reaction vessel 3. Molten magnesium 12 collects and floats above the magnesium chloride due to the difference in their densities and the magnetic field by electromagnetic induction, so that it remains separate from the magnesium chloride. Part of the molten magnesium chloride flows into the gap between the titanium ingot 11 and the inner surface of the reaction vessel 3 where it solidifies by cooling, to give pressure sealing and electrical insulation actions.

Subsequently, more argon gas is introduced into the reaction vessel 3 to increase the pressure, and liquid magnesium and titanium tetrachloride are fed through the magnesium feed pipe 6 and the titanium tetrachloride feed pipe 7 connected to the top of the reaction vessel 3 to the surface of the molten magnesium 12, forming an upper layer of the molten bath or the reaction zone. Alternatively, the magnesium feed pipe 6 may be connected to the side of the reaction vessel 3 as in the apparatus of Figure 1.

Titanium tetrachloride in the reaction zone or at the surface of the molten magnesium layer of the molten bath reacts in liquid form with the liquid magnesium to produce titanium 14 and magnesium chloride 13. Alternatively, it may react as vapour with magnesium vapour vapourised from the molten magnesium layer or with liquid magnesium.

The heat of reaction and the effect of the heater 8 cause the temperature of the molten bath in the reaction vessel 3 to rise above the melting point of titanium. However, the reaction vessel 3 is kept at a pressure above a vapour pressure of magnesium at that temperature, so that the titanium product 14, the magnesium chloride by-product 13 and the magnesium 12 are all kept in a liquid state. Also, the molten bath is vertically separated into three layers, namely, magnesium 12, magnesium chloride 13 and titanium 14, in that order, due to the differences in their densities.

The molten metallic titanium product 14 precipitates and sinks through the molten magnesium layer and the molten magnesium chloride layer to the bottom of the reaction vessel 3 and reaches the top of the titanium ingot 11, where it remains in the molten state and is subjected to stirring and mixing by the lower electromagnetic induction heating coil 8b. This results in the molten titanium product 14 being homogeneous.

The titanium product 14 coalesces with the top of the titanium ingot 11 and the titanium ingot 11 is continuously drawn out at a suitable rate, during which the product is cooled and solidified by the cooling agent circulated in the cooling pipes 33 of the segments 32.

The magnesium chloride by-product 13 is discharged through the discharge pipe 9 connected to the side of the reaction vessel 3 at a discharge rate which is adjusted so that the molten bath at the reaction zone is kept at a constant level. At this time, a part of the magnesium chloride flows into the gap between the titanium ingot 11 and the wall of the reaction vessel and solidifies there to form an insulating layer which serves to prevent contact between the ingot 11 and the reaction vessel. The insulating layer exhibits heat insulating and pressure sealing actions. The insulating layer may be partially broken by mechanical friction when the titanium ingot 11 is downwardly drawn out, however, when this happens, the magnesium chloride rapidly flows from the molten magnesium chloride phase into the broken portion of the insulating layer and solidifies to re-form an insulating layer. Also, the molten titanium is heated by the lower electromagnetic induction heating coil 8b and tends to levitate at its central portion. Accordingly, magnesium chloride readily flows into the gap between the wall of the reaction vessel and the titanium ingot 11 to facilitate formation of the additional insulating layer.

The titanium ingot 11 is drawn out at a rate corresponding to the amount of titanium precipitated on the titanium ingot by precipitation by means of rollers (not shown). Accordingly, the position of the molten titanium product above the titanium ingot 11 is kept substantially constant. A part of heat of reaction in the reaction vessel is removed upwards from the reaction vessel 3 by radiation and convection, however, a large part of the

heat is removed outwardly by the cooling agent circulated in the circulation pipes 33 at the segments 32 constituting the reaction vessel 3.

Accordingly, the present invention is carried out under conditions where the temperature of the reaction zone is kept above the melting point of the metallic titanium product and its pressure is kept at least at the vapour pressure of the reducing metal agent at that temperature, so that boiling of the reducing metal agent and its chloride may be substantially prevented to keep them in a liquid state in the reaction vessel, resulting in the reduction being carried out efficiently.

The present invention also allows the metallic titanium to be produced in the form of a liquid if preferred. The separation of the metallic titanium product and the chloride by-product of the reducing metal agent is simple, as is the recovery of the by-product, and the titanium ingot may be directly removed, enabling the whole production apparatus to be small-sized.

Furthermore, the present invention permits production of metallic titanium to be continuously carried out, so that the separating, crushing and melting steps required in the conventional Kroll process may be eliminated, leading to a significant decrease in producing costs while providing titanium of the highest quality.

The above description has been made in connection with manufacturing titanium. However, the present invention can also be applied to production of metals such as zirconium, hafnium, niobium and their alloys, silicon, and the like.

The present invention will now be illustrated with reference to the following non-limiting Examples.

#### EXAMPLE 1

The example was carried out using an apparatus constructed in accordance with Figure 1.

A reaction vessel having an inner diameter of 20cm was used and a titanium ingot having an inner diameter of 10cm was inserted into the mould section of the reaction vessel to close the bottom. 20kg magnesium chloride and 4.6kg magnesium were charged into the reaction vessel, which was then fully closed.

The atmosphere in the reaction vessel was replaced with argon, the magnesium chloride and magnesium were heated to 1000°C by electromagnetic induction heating and the reaction vessel was pressurised to about 50atms.

Immediately after such conditions were established, titanium tetrachloride and liquid magnesium kept at 800°C were supplied to the reaction vessel at feed rates of 4.0ℓ/min (7.0kg/min) and 1.2ℓ/min (1.8kg/min), respectively. This caused a temperature of the bath to rise rapidly to 1827°C, and so the power for the electromagnetic induction heating was decreased to keep the temperature at 1827°C ± 50°C.

Subsequently, the ingot was drawn out downwardly at an average velocity of 4.9cm/min. The operation was continued for 3 hours, resulting in a titanium ingot being manufactured in an amount of 0.3 tonne.

The magnesium chloride by-product produced during the operation was continuously discharged from the reaction vessel at the appropriate rate to keep the depth of the bath in the reaction vessel constant.

The titanium ingot so produced was compared to sponge titanium produced by the Kroll process. It was found that the titanium ingot had a high purity and quality as indicated in Table 1, in which the figures are in wt% and the balance is titanium in each case.



Table 1

Type	Chemical Composition										
	O	C	H	N	Si	Fe	Al	Cr	Ni	Cu	Sn
Present Invention	0.010	0.005	$\geq 0.001$	0.001	0.007	$\geq 0.010$	0.005	$\geq 0.001$	$\geq 0.005$	0.005	0.01
Sponge Ti by Kroll Method	$\geq 0.06$	$\geq 0.01$	$\geq 0.003$	$\geq 0.01$	$\geq 0.02$	$\geq 0.05$	$\geq 0.03$	$\geq 0.01$	$\geq 0.02$	$\geq 0.005$	$\geq 0.02$

The Symbol  $\geq$  is used to mean "up to and including", so that the following figure is a maximum value

## EXAMPLE 2

This example was carried out using an apparatus constructed in accordance with Figures 2 and 3.

A reaction vessel having an inner diameter of 20cm was used and a titanium ingot having an inner diameter of 19.5cm was inserted into the mould section of the reaction vessel to close the bottom. Then, 20kg magnesium chloride and 4.6 kg magnesium were charged into the reaction vessel, which was then fully closed.

The atmosphere in the reaction vessel was replaced with argon and the top of the titanium ingot and the reaction vessel were heated by electromagnetic induction heating to heat the magnesium chloride and magnesium in the reaction zone to a temperature of 1000°C. Magnesium chloride melted by the heating flowed into the gap between the wall of the reaction vessel and the titanium ingot to form an insulating layer which also exhibited a pressure sealing action.

The reaction vessel was then pressurised to about 50atms. Immediately after such conditions were attained, titanium tetrachloride and liquid magnesium kept at 800°C were supplied to the reaction vessel at feed rates of 4.0l/min (7.0kg/min) and 1.2l/min (1.8kg/min), respectively. This caused the temperature of the bath to rise rapidly to 1827°C, and so the power for the electromagnetic induction heating was decreased to keep the temperature of 1827°C  $\pm$  50°C.

Subsequently, the ingot was drawn out downwardly at an average velocity of 1.3cm/min. The operation was continued for 2 hours, resulting in titanium ingot being manufactured in an amount of 0.2 tonne.

The magnesium chloride by-product produced during the operation was continuously discharged from the reaction vessel at the appropriate rate to keep the depth of the bath in the reaction vessel constant.

The titanium ingot so produced was compared to sponge titanium produced by the Kroll process. It was found that the titanium ingot had a high purity and quality similar to that shown in Table 1.

## Claims

1. A method for producing titanium by the reduction of titanium tetrachloride with a reducing metal agent characterised by the steps of: maintaining the temperature and pressure in a reaction zone (12) in a reaction vessel (3) above the melting point of the metallic titanium (14) to be produced and above the vapour pressure of the reducing metal agent at that temperature; supplying titanium tetrachloride and the reducing metal agent to the reaction vessel (3) to react to produce a metallic titanium product (14) and a chloride by-product (13) of the reducing metal agent while maintaining the product and the by-product in a molten state; separating the metallic titanium product (14) and the chloride by-product (13) of the reducing metal agent from each by making use of the differences in their densities; collecting the metallic titanium product (14) at the bottom of the reaction vessel (3); and continuously drawing off the metallic titanium product (14) from the bottom of the reaction vessel (3).

2. A method as claimed in Claim 1 characterised in that the titanium product (14) is solidified by cooling as it is withdrawn.

3. A method as claimed in Claim 1 characterised in that a molten bath (12) of chloride of the reducing metal agent and optionally also of the reducing metal agent is previously formed in the reaction vessel so that the surface of the molten bath constitutes the reaction zone and titanium tetrachloride and the reducing metal agent are supplied to the reaction zone.

4. A method as claimed in Claim 3, characterised in that the titanium tetrachloride is supplied as a liquid from the top of the reaction vessel (3) and the reducing metal agent is supplied either in the same way or is injected into the bath (12).

5. A method as claimed in any preceding claim characterised in that the chloride by-product (13) of the reducing metal agent is discharged (9) from the reaction vessel at a rate arranged to maintain the position of the reaction zone (12) substantially constant.

6. A method as claimed in any preceding claim characterised by the steps of inserting a titanium ingot (11) into the bottom of the reaction vessel (3) resulting in the coalescence of the metallic titanium metal product (14) with the titanium ingot (11) and drawing the metallic titanium product (14) out continuously together with the titanium ingot (11) at a rate corresponding to the amount of the metallic titanium product being coalesced with the titanium ingot.

7. A method as claimed in any preceding claim characterised in that the reducing metal agent is magnesium or sodium.

8. A method as claimed in any preceding claim, characterised in that the reaction pressure is above the total sum of the vapour pressures of the reducing metal agent and its chloride at the reaction temperature.

9. A method for producing a metal by the reduction of a polyhalide of the metal with a reducing metal agent characterised by the steps of: maintaining the temperature and pressure in a reaction zone (12) in a reaction vessel (3) above the melting point of the metal (14) to be produced and above the vapour pressure of the reducing metal agent at that temperature; supplying the polyhalide of the product metal

and the reducing metal agent to the reaction vessel (3) to react to produce the product metal (14) and a halide by-product (13) of the reducing metal agent while maintaining the product and the by-product in a molten state; separating the product metal (14) and the halide by-product (13) of the reducing metal agent from each by making use of the differences in their densities; collecting the product metal (14) at the bottom of the reaction vessel (3); and continuously drawing off the product metal (14) from the bottom of the reaction vessel (3).

10. An apparatus for producing metallic titanium by the reduction of titanium tetrachloride with a reducing metal agent characterised by: a reaction vessel (3) having a reaction zone (12) in which a temperature above a melting point of the titanium product (14) is defined and which is kept at a pressure sufficient to prevent boiling of the reducing metal agent and its chloride (13) at that temperature; a reducing metal agent feed pipe (6) for supplying the reducing metal agent in the form of a liquid from the side or the top of the reaction vessel (3) to the reaction zone; a titanium tetrachloride feed pipe (7) for supplying titanium tetrachloride from the top of the reaction vessel (3) to the reaction zone; a discharge pipe (9) for discharging the chloride by-product of the reducing metal agent from the side of the reaction vessel; heating means (8) positioned outside the reaction vessel (3) at a position corresponding to the reaction zone (12); and a withdrawal section (10) at the bottom of the reaction vessel (3) for continuously drawing out the metallic titanium product (14).

11. An apparatus as claimed in Claim 10 characterised in that the withdrawal section is a mould section (10) at the bottom of the reaction vessel (3) for solidifying the molten metallic titanium product (14) by cooling as it is continuously drawn out from the reaction vessel (3).

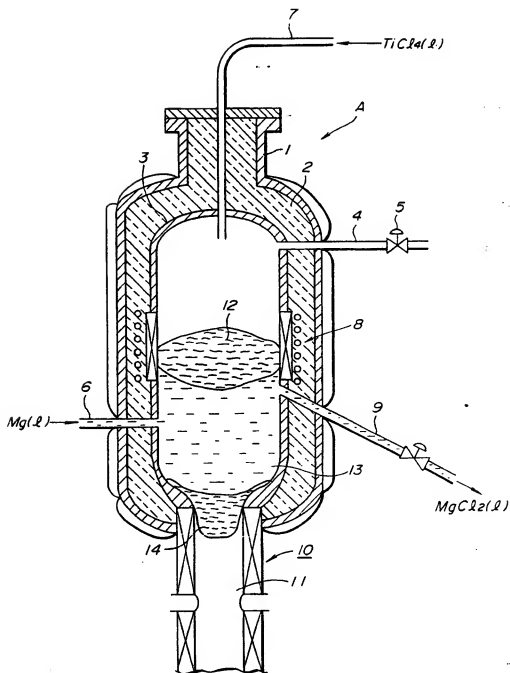
12. An apparatus as claimed in Claim 11 characterised by cooling means (33-35) located in the wall of the reaction vessel (3) for circulating a cooling agent at least from the reaction zone (12) to the mould section (10).

13. An apparatus as claimed in Claim 11 or Claim 12 characterised by heating means (8) arranged on portions of the outer periphery of the reaction vessel at positions corresponding to the reaction zone (12) and the mould section (1).

14. An apparatus as claimed in any of Claims 10 to 13 characterised in that the reaction vessel (3) comprises a plurality of longitudinal segments (22) separated by slits (31) thereby dividing the reaction vessel (3) in its longitudinal direction each of the slits (31) being filled with an electrically insulating and heat resistant material.

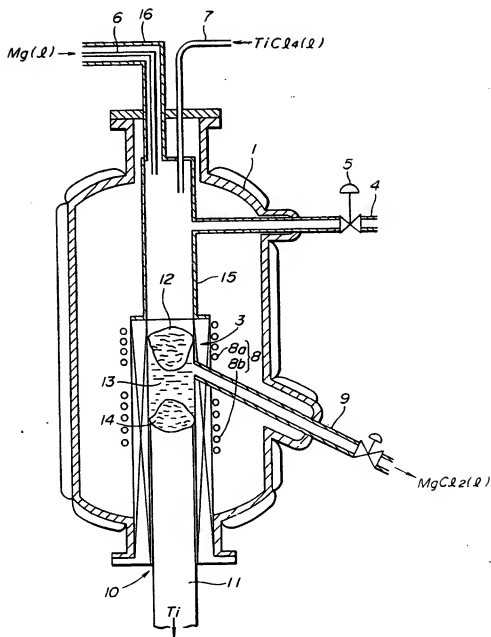
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FIG.1



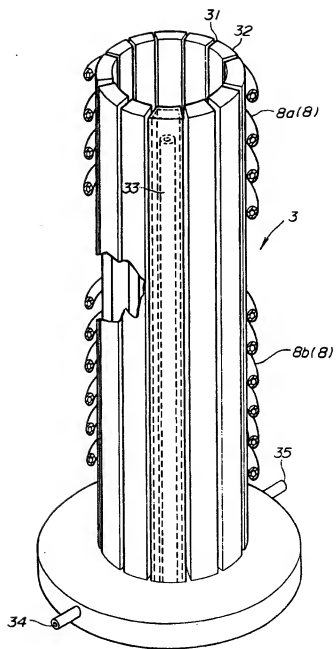
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**FIG. 2**



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**FIG. 3**





European Patent  
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# EUROPEAN SEARCH REPORT

Application Number

EP 88 30 6510

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X	US-A-3 847 596 (G.W. HOLLAND et al.) * claim 1 * & JP - B - 46 19761 (Cat. D)	1, 9	C 22 B 34/12 C 22 B 5/04
A	FR-A-2 461 014 (COCKERILL) * claim 1 * & JP - A - 56 35733 (Cat. D)	1	
A	US-A-4 442 082 (A. SANJURJO) * claim 1 *	9	
A	US-A-2 816 828 (M. BENEDICT et al.)		
A	PATENT ABSTRACTS OF JAPAN, vol. 9, no. 228 (C-303)[1951], 13th September 1985; & Jp - A - 60 89529 (MITSUBISHI KINZOKU K.K.) 20-05-1985		
A, D	US-A-3 775 091 (P.G. CLITES et al.)		
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 22 B 34/12 C 22 B 5/04
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
BERLIN		29-08-1988	SUTOR W
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(54) Method for preparing an article having dispersoid distributed in a metallic matrix

(57) An article has a metallic matrix made of its constituent elements with a dispersoid distributed therein. The article is prepared by furnishing (50) at least one nonmetallic matrix precursor compound. All of the non-metallic matrix precursor compounds collectively include the constituent elements of the metallic matrix in their respective constituent-element proportions. A mixture of an initial metallic material and the dispersoid is produced (52). The matrix precursor compounds are

chemically reduced to produce the initial metallic material, without melting the initial metallic material, and the dispersoid is distributed in the initial metallic material. The mixture of the initial metallic material and the dispersoid is consolidated (54) to produce a consolidated article having the dispersoid distributed in the metallic matrix comprising the initial metallic material. The initial metallic material, the dispersoid, and the consolidated article are not melted during the consolidation.

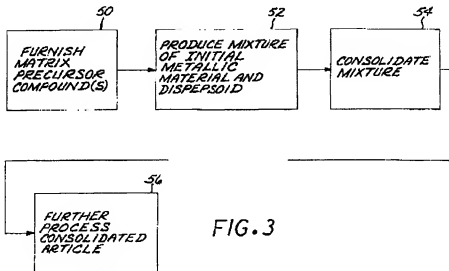


FIG. 3



## Description

[0001] This invention relates to the preparation of a material in which a dispersoid is dispersed through a metallic matrix, and more particularly to the preparation of such a material that avoids any melting of the constituents.

[0002] Materials having a dispersion of substantially inert dispersoids distributed in a metallic matrix are known. An example is TD-nickel, in which thorium oxide dispersoid is distributed through a nickel matrix. The dispersoids improve the mechanical properties of the material by interfering with dislocation movement, particularly if the dispersoids are closely spaced, and also by inhibiting the movement of the grain boundaries of the matrix during elevated temperature exposure.

[0003] There are two primary techniques for producing such materials, mechanical alloying and spray forming. In mechanical alloying, the more widely used of the two approaches, the material of the metallic matrix is melted and solidified as a powder. One or more types of metallic powders are mixed with the dispersoid, and the mixture is mechanically deformed in a high-energy environment such as a ball mill. In the mechanical deformation, the largely nondeformable dispersoid is incorporated into the deformable metallic powder(s) by repeated fracturing and cold welding of the metallic powder particles with the dispersoid contained at the welded interfaces. After the mechanical deformation, the mixture is consolidated. This approach requires lengthy and/or costly ball milling operations which can be prone to the introduction of defects into the mechanically alloyed material. Additionally, many metallic matrix materials that are otherwise of interest cannot be used in mechanical alloying, because they are not sufficiently malleable to cold weld to the dispersoids in the ball milling. The use of mechanical alloying is therefore limited primarily to lower-strength, higher-ductility metallic materials.

[0004] In spray forming, metallic material is melted and sprayed from a spray gun to solidify or partially solidify in a suitable inert atmosphere prior to being consolidated against a substrate. The dispersoid is added to the spray of the metallic material as it leaves the spray gun and is thereby mixed with the solidified metal. Spray forming can only be used in specialized circumstances, inasmuch as the process is limited to the use of dispersoids that do not react with or melt in the molten metal, the process is expensive, and it is difficult to control the size and spacing of the dispersoid. The microstructure is dominated by the solidification structure of the metallic material produced at rapid cooling rates.

[0005] There is a need for an improved approach to the preparation of articles having a metallic matrix with dispersoids distributed therein. The required improvements include reducing the manufacturing time, reducing the number of process steps, reducing the sources of contamination, and permitting the use of higher

strength matrix materials in combination with fine dispersoids. The present invention fulfills this need, and further provides related advantages.

[0006] The present invention provides a technique for preparing an article having a metallic alloy matrix with a fine dispersoid distributed therein. The article is preferably prepared without melting of the metal alloy and without mechanical deformation of the metal alloy, prior to final consolidation and mechanical forming. The incidence of defects in the metallic matrix is thereby greatly reduced, as compared with mechanical alloying. The present approach allows the use of higher-strength metallic matrix materials than possible with mechanical alloying, and the use of different dispersoids than are possible with prior approaches. There is less anisotropy in the final article, and a fine grain structure can be achieved in the final article. The cost of manufacturing the article by the present approach is less than with prior approaches.

[0007] An article has a metallic matrix made of its constituent elements with a dispersoid distributed therein. The article is prepared by furnishing at least one non-metallic matrix precursor compound. All of the non-metallic matrix precursor compounds collectively include the constituent elements of the metallic matrix in their respective constituent-element proportions. A mixture of an initial metallic material and the dispersoid is produced. The matrix precursor compounds are chemically reduced to produce the initial metallic material, without melting the initial metallic material, and the dispersoid is distributed in the initial metallic material. The mixture of the initial metallic material and the dispersoid is consolidated to produce a consolidated article having the dispersoid distributed in the metallic matrix comprising the initial metallic material. The initial metallic material, the dispersoid, and the consolidated article are not melted during the consolidation. Preferably, there is no mechanical deformation. The initial metallic material and the matrix of the final article may be of any operable constituents. The present approach is operable, for example, with nickel-base, iron-base, cobalt-base, titanium-base, magnesium-base, and aluminum-base materials.

[0008] The dispersoids may be introduced into and mixed with the metallic component in any operable manner. In one preferred approach, the step of producing includes the steps of furnishing the dispersoids, and mixing the dispersoids with the matrix precursor compounds prior to or concurrently with the step of chemically reducing. In another preferred approach, the step of producing includes the steps of furnishing the dispersoids, and mixing the dispersoids with the initial metallic material after the step of chemically reducing. In another preferred approach, the step of producing includes the steps of furnishing a dispersoid-precursor, and mixing the dispersoid precursor with the matrix precursor compound prior to or concurrently with the step of chemically reducing, and wherein the dispersoid precursor chemically reacts during the step of chemically reacting to pro-

duce the dispersoid. In another preferred approach, an element of the dispersoid may be supplied as a precursor compound to be reduced in a second reduction step and then reacted to form the desired dispersoid compound.

[0009] The matrix precursor compounds may be furnished in any operable physical form. For example, a compressed mass of the matrix precursor compounds may be furnished. Typically, such a compressed mass is larger in dimensions than the consolidated article. The matrix precursor compounds may instead be furnished in an uncompressed, free-flowing form of finely divided particles, or a liquid, or a vapor.

[0010] The chemical reduction may be performed by any operable approach, such as solid-phase reduction or vapor-phase reduction. The chemical reduction may produce the initial metallic material in any operable form. For example, the step of chemically reducing may produce a sponge of the initial metallic material, or particles of the

[0011] The consolidation may be performed by any operable approach, such as, for example, hot isostatic pressing, forging, pressing and sintering, and containerized extrusion. After consolidation, the consolidated article may be formed, heat treated, or otherwise final processed.

[0012] The present approach produces an article that has a metallic matrix and dispersoids uniformly distributed in the bulk of the metallic matrix, or with a high concentration near the surface if desired. A wide variety of metallic materials and dispersoid materials may be used. The dispersoids may be, for example, oxides, carbides, nitrides, borides, or sulfides, or combinations of the constituent elements, such as carbonitrides, formed with the elements of the metallic matrix or with other intentionally added elements. The dispersoids are selected to be either thermodynamically stable (non-reducible) compared to the matrix alloy, or too chemically inert and stable to be reduced by the process that reduces the matrix precursor compounds. The dispersoid is introduced at a point in the processing where it is stable with respect to all subsequent processing steps. The metallic matrix is never melted during the preparation processing, so that there is little if any chemical reaction between the metallic components and the dispersoid. In the preferred approach, there is no high-energy or other deformation of the metallic material prior to consolidation, so that there is a greatly reduced incidence of the mechanical and heating defects that are associated with mechanical alloying. Additionally, because the introduction of the dispersoid does not depend upon the mechanical deformation of the matrix material, the present approach may be used with a broader range of useful metallic alloy systems than possible with mechanical alloying. High-strength alloys that are not amenable to extensive mechanical deformation may be produced with a distribution of the dispersoid therein by the present approach but not by mechanical alloying. New types of

dispersoids may also be used. Those dispersoids may be added as the dispersoid compound, or in some cases may be added as elements or precursor compounds that react with the matrix alloy to form the dispersoids.

5 Alternatively, the precursor compound may react with other components in a separate reaction step.

[0013] Other features and advantages of the present invention will be apparent from the following more detailed description of the preferred embodiment, taken in conjunction with the accompanying drawings, which illustrate, by way of example, the principles of the invention, and in which:

Figure 1 is a perspective view of an article made by the present approach;

Figure 2 is an idealized microstructure of the article of Figure 1;

Figure 3 is a block flow diagram of a preferred approach for practicing the invention;

Figure 4 is an idealized microstructure of the metallic article, after some reaction that produces a uniform dispersion;

Figure 5 is an idealized microstructure of the metallic article, after inward diffusion of a reactant during heat treatment or service; and

Figure 6 is an idealized microstructure of a conventional metallic article, after inward diffusion of the reactant.

35 [0014] Figure 1 depicts a component article 20 of a gas turbine engine such as a compressor blade 22. The compressor blade 22 is preferably formed of a titanium-base alloy having a dispersoid therein, as will be discussed in greater detail. The compressor blade 22 includes an airfoil 24 that acts against the incoming flow of air into the gas turbine engine and axially compresses the air flow. The compressor blade 22 is mounted to a compressor disk (not shown) by a dovetail 26 which extends downwardly from the airfoil 24 and engages a slot on the compressor disk. A platform 28 extends longitudinally outwardly from the area where the airfoil 24 is joined to the dovetail 26.

45 [0015] A titanium-base alloy having a dispersoid therein is one preferred application of the present approach, and it will be used to illustrate specific embodiments. However, the present approach is not limited to titanium-based alloys with dispersoids therein, and is applicable to other types of metallic alloys with dispersoids therein.

55 [0016] Figure 2 is an idealized depiction of the microstructure 30 of the article 20. The microstructure 30 includes grains 32 of a metallic matrix 34 with grain boundaries 36 separating the grains 32. The metallic matrix

comprises its alloy constituent elements. A dispersoid 38 in the form of a plurality of dispersoid particles is distributed in the metallic matrix 34. The dispersoid 38 may include grain-boundary dispersoid particles 40 that reside along the grain boundaries 36, and interior dispersoid particles 42 that reside within the grains 32. The grain-boundary dispersoid particles 40 serve to limit grain growth during elevated-temperature exposure, and the interior dispersoid particles 42 serve to restrict dislocation movement to increase the alloy's strength, most specifically the creep resistance. Examples of suitable dispersoids include, for example, oxides, carbides, nitrides, borides, or sulfides, formed with the elements of the metallic matrix or with other intentionally added elements. The dispersoids may be simple chemical forms. The dispersoids may instead be more complex, multicomponent compounds such as, for example, carbonitrides or multicomponent oxides such as  $Y_2O_3$ - $Al_2O_3$ -based oxides. Such dispersoids include an element (or elements) selected from the group consisting of oxygen, carbon, nitrogen, boron, sulfur, and combinations thereof. The dispersoids are either thermodynamically stable (non-reducible) compared to the matrix alloy, or too chemically inert to be reduced by the process that reduces the matrix precursor compounds. The dispersoid is introduced at a point in the processing where it is stable with respect to all subsequent processing steps. That is, if a particular type of dispersoid is unstable with respect to some earlier processing step, it is introduced only after that processing step is

**[0017]** The dispersoid 38 (including both grain-boundary dispersoid particles 40 and interior dispersoid particles 42) may be present in any amount. However, the dispersoid 38 is preferably present in an amount sufficient to provide increased strength to the article 20 by inhibiting dislocation movement in the metallic matrix 34, by acting as a composite-material strengthener, and/or by inhibiting movement of the grain boundaries 36. The volume fraction of dispersoid 38 required to perform these functions varies depending upon the nature of the matrix 34 and the dispersoid 38, but is typically at least about 0.5 percent by volume of the article, and more preferably at least about 1.5 percent by volume of the article. To achieve these volume fractions, the elements that react to form the dispersoid 38 must be present in a sufficient

**[0018]** Figure 3 is a block flow diagram illustrating a preferred method for producing the article 20. At least one nonmetallic matrix precursor compound is furnished, step 50. As used herein, the term "metallic alloy" includes both conventional metallic alloys and intermetallic compounds formed of metallic constituents, such as approximately equiatomic TiAl. Relatively small amounts of nonmetallic elements, such as boron, carbon, and silicon, may also be present. All of the nonmetallic matrix precursor compounds collectively include the constituent elements of the metallic matrix in their respective constituent-element proportions. (The dis-

persoid or its precursor is supplied separately, as will be discussed.) The metallic elements may be supplied by the matrix precursor compounds in any operable way. In the preferred approach, there is exactly one precursor compound for each alloying element, and that one precursor compound provides all of the material for that respective metallic constituent in the alloy. For example, for a four-element metallic matrix material that is the final result of the process, a first precursor compound supplies all of the first element, a second precursor compound supplies all of the second element, a third precursor compound supplies all of the third element, and a fourth precursor compound supplies all of the fourth element. Alternatives are within the scope of the approach, however. For example, several of the precursor compounds may together supply all of one particular metallic element. In another alternative, one precursor compound may supply all or part of two or more of the metallic elements. The latter approaches are less preferred, because they make more difficult the precise determination of the elemental proportions in the final metallic material.

**[0019]** The metallic matrix 34 and its constituent elements comprise any operable type of alloy. Examples include a nickel-base material, an iron-base material, a cobalt-base material, a titanium-base material, a magnesium-base material, and an aluminum-base material. An "X-base" alloy has more of element X than any other element.

**[0020]** The matrix precursor compounds are nonmetallic and are selected to be operable in the reduction process in which they are reduced to metallic form. In one reduction process of interest, solid-phase reduction, the precursor compounds are preferably metal oxides. In another reduction process of interest, vapor-phase reduction, the precursor compounds are preferably metal halides. Mixtures of different types of matrix precursor compounds may be used, as long as they are operable in the subsequent chemical reduction.

**[0021]** The nonmetallic precursor compounds are selected to provide the necessary alloying elements in the final metallic article, and are mixed together in the proper proportions to yield the necessary proportions of these alloying elements in the metallic article. For example, if the final article were to have particular proportions of titanium, aluminum, vanadium, erbium, and oxygen in the ratio of 88.5:6:4:3:0.5 by weight, the nonmetallic precursor compounds are preferably titanium oxide, aluminum oxide, vanadium oxide, and erbium oxide for solid-phase reduction. The final oxygen content is controlled by the reduction process as discussed subsequently. Nonmetallic precursor compounds that serve as a source of more than one of the metals in the final metallic article may also be used. These precursor compounds are furnished and mixed together in the correct proportions such that the ratio of titanium:aluminum:vanadium:erbium in the mixture of precursor compounds is that required to form the metallic alloy in the final ar-

title.

[0022] A mixture of an initial metallic material and the dispersoid is produced, step 52. As part of the producing step 52, the single nonmetallic precursor compound or the mixture of nonmetallic precursor compounds is chemically reduced to produce the initial metallic material, without melting the initial metallic particles. As used herein, "without melting", "no melting", and related concepts mean that the material is not macroscopically or grossly melted for an extended period of time, so that it liquefies and loses its shape. There may be, for example, some minor amount of localized melting as low-melting-point elements melt and are diffusively alloyed with the higher-melting-point elements that do not melt, or very brief melting for less than about 10 seconds. Even in such cases, the gross shape of the material remains.

[0023] In one preferred reduction approach, termed vapor-phase reduction because the nonmetallic precursor compounds are furnished as vapors or gaseous phase, the chemical reduction may be performed by reducing mixtures of halides of the base metal and the alloying elements using a liquid alkali metal or a liquid alkaline earth metal. For example, titanium tetrachloride and the halides of the alloying elements are provided as gases. A mixture of these gases in appropriate amounts is contacted to molten sodium, so that the metallic halides are reduced to the metallic form. The metallic alloy is separated from the sodium. This reduction is performed at temperatures below the melting point of the metallic alloy. The approach is described more fully in US Patents 5,779,761 and 5,958,106.

[0024] Reduction at lower temperatures rather than higher temperatures is preferred. Desirably, the reduction is performed at temperatures of 600°C or lower, and preferably 500°C or lower. By comparison, prior approaches for preparing specific metallic alloys often reach temperatures of 900°C or greater. The lower-temperature reduction is more controllable, and also is less subject to the introduction of contamination into the metallic alloy, which contamination in turn may lead to chemical defects. Additionally, the lower temperatures reduce the incidence of sintering together of the particles during the reduction step.

[0025] In this vapor-phase reduction approach, a nonmetallic modifying element or compound presented in a gaseous form may be mixed into the gaseous nonmetallic precursor compound prior to its reaction with the liquid alkali metal or the liquid alkaline earth metal. In one example, oxygen or nitrogen may be mixed with the gaseous nonmetallic matrix precursor compound(s) to increase the level of oxygen or nitrogen, respectively, in the initial metallic material. It is sometimes desirable, for example in a titanium-base alloy, that the oxygen content of the initial metallic particle and the final metallic article be about 1200-2000 parts per million by weight to strengthen the final metallic article or to provide oxygen that is used in forming the dispersoid. Rather than

adding the oxygen in the form of solid titanium dioxide powder, as is sometimes practiced for titanium-base alloys produced by conventional melting techniques, the oxygen is added in a gaseous form that facilitates mixing and minimizes the likelihood of the formation of hard alpha phase in the final article. When the oxygen is added in the form of titanium dioxide powder in conventional melting practice, agglomerations of the powder may not dissolve fully, leaving fine particles in the final metallic article that constitute chemical defects. The present approach avoids that possibility. For other alloy systems, lower oxygen, nitrogen, etc. content may also be beneficial. Similarly, elements such as sulfur and carbon may be added using appropriate gaseous compounds of these elements. Complex combinations of such gaseous elements may be provided and mixed together, such as gaseous compounds of oxygen, nitrogen, sulfur, and/or carbon, leading to the formation of chemically more-complex dispersoids.

[0026] In another reduction approach, termed solid-phase reduction because the nonmetallic matrix precursor compounds are furnished as solids, the chemical reduction may be performed by fused salt electrolysis. Fused salt electrolysis is a known technique that is described, for example, in published patent application WO 99/64638. Briefly, in fused salt electrolysis the mixture of nonmetallic matrix precursor compounds, furnished in a finely divided solid form, is immersed in an electrolysis cell in a fused salt electrolyte such as a chlorides salt at a temperature below the melting temperature of the alloy that forms from the nonmetallic matrix precursor compounds. The mixture of nonmetallic matrix precursor compounds is made the cathode of the electrolysis cell, with an inert anode. The elements combined with the metals in the nonmetallic matrix precursor compounds, such as oxygen in the preferred case of oxide nonmetallic matrix precursor compounds, are partially or completely removed from the mixture by chemical reduction (i.e., the reverse of chemical oxidation). The reaction is performed at an elevated temperature. The cathodic potential is controlled to ensure that the reduction of the nonmetallic matrix precursor compounds will occur, rather than other possible chemical reactions such as the decomposition of the molten salt. The electrolyte is a salt, preferably a salt that is more stable than the equivalent salt of the metals being refined and ideally very stable to remove the oxygen or other gas to a desired low level. The chlorides and mixtures of chlorides of barium, calcium, cesium, lithium, strontium, and yttrium are preferred. The chemical reduction is preferably, but not necessarily, carried to completion, so that the nonmetallic matrix precursor compounds are completely reduced. Not carrying the process to completion is a method to control the oxygen content of the metal produced.

[0027] In another reduction approach, termed "rapid plasma quench" reduction, the precursor compound such as titanium chloride is dissociated in a plasma arc

at a temperature of over 4500°C. The precursor compound is rapidly heated, dissociated, and quenched in hydrogen gas. The result is fine metallic-hydride particles. Any melting of the metallic particles is very brief, on the order of 10 seconds or less, and is within the scope of "without melting" and the like as used herein. The hydrogen is subsequently removed from the metallic-hydride particles by a vacuum heat treatment. Oxygen or other gas (e.g., nitrogen) may also be added to react with the stable-dispersoid-forming additive elements to form the stable dispersion.

[0028] The dispersoid 38 in the form of the dispersoid particles is introduced during the producing step 52. The dispersoid 38 may be of any operable type. The dispersoid 38 be furnished in its final form, or it may be furnished as a precursor that is reacted to produce the final form of the dispersoid. The selection of the dispersoid 38 is made in conjunction with the type of matrix alloy and the requirements of the final article. Some examples of the dispersoids may be oxides, carbides, nitrides, borides, or sulfides, or combinations thereof, such as carbonitrides, formed with the elements of the metallic matrix or with other intentionally added elements.

[0029] Four approaches for introducing the dispersoid 38 are of particular interest. In a first approach, the dispersoids are furnished in essentially their final form and are mixed with the matrix precursor compounds prior to or concurrently with the step of chemically reducing. That is, the mixture of matrix precursor compounds and dispersoids is given the chemical reduction treatment, but only the matrix precursor compounds are actually reduced. The dispersoids are selected to be either thermodynamically stable (non-reducible) compared to the matrix alloy, or too chemically inert to be reduced by the process that reduces the matrix precursor compounds. The dispersoid is introduced at a point in the processing where it is stable with respect to all subsequent processing steps.

[0030] In a second approach, the dispersoids are furnished but not subjected to the chemical reduction treatment. Instead, they are mixed with the initial metallic material that results from the chemical reduction step, but after the step of chemically reducing is complete. This approach is particularly effective when the step of chemically reducing is performed on a flowing powder of the matrix precursor compounds, but it also may be performed on a precompacted mass of the matrix precursor compounds, resulting in a spongy mass of the initial metallic material. The dispersoids 38 are received onto the surface of the powder or on the surface of, and into the porosity of, the spongy mass.

[0031] In a third approach, a dispersoid-precursor is furnished, rather than the final precursor. The dispersoid precursor is mixed with the matrix precursor compound prior to or concurrently with the step of chemically reducing. The dispersoid precursor chemically reacts with another element or elements during the step of chemically reacting to produce the dispersoid. For example,

the dispersoid-precursor could be an oxide former such as magnesium, calcium, scandium, thorium, and yttrium, and rare earths such as lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium, and mixtures thereof, which react with excess oxygen during the chemical reduction to produce oxide dispersoids.

[0032] In a fourth approach, the matrix precursor is first produced as powder particles, or as a sponge by compacting the precursor compounds of the metallic elements. The particles or sponge is then first chemically reduced. The dispersoid is thereafter produced at the surfaces (external and internal, if the particles are spongelike) of the particles, or at the external and internal surfaces of the sponge. In one approach, the particles or sponge is dipped into a solution of a precursor compound of the dispersoid, such as an erbium chloride solution, to coat the surfaces of the particles or the sponge. The precursor compound of the dispersoid is second chemically reduced to produce the first element of the dispersoid, such as erbium, at the surfaces of the particles or at the surfaces of the sponge. The element of the dispersoid is then chemically reacted (for example, oxidized) to produce the dispersoid, erbium oxide in the example, distributed over the surfaces of the particles or the sponge. Upon the subsequent consolidation, discrete dispersoids are distributed throughout the consolidated and compacted article. In some cases the oxidation may be performed during or integral with the consolidation process. The dispersoid may also be broken into smaller pieces in the consolidation process and distributed further through the metallic matrix.

[0033] Whatever the reduction technique used in step 52 and however the dispersoid is introduced, the result is a mixture of an initial metallic material and the dispersoid. The initial metallic material may be free-flowing particles in some circumstances, or have a sponge-like structure in other cases. The sponge-like structure is produced in the solid-phase reduction approach if the matrix precursor compounds have first been compacted together prior the commencement of the actual chemical reduction. The matrix precursor compounds may be compressed to form a compressed mass that is larger in dimensions than a desired final metallic article.

[0034] The mixture of the initial metallic material and the dispersoid is thereafter or concurrently consolidated to produce a consolidated article, step 54, without melting the initial metallic material, without melting the dispersoid, and without melting the consolidated article. The consolidation step 54 may be performed by any operable technique, with examples being hot isostatic pressing, forging, pressing and sintering, and containerized extrusion.

[0035] It is preferred that there be no mechanical deformation of initial metallic material and/or the mixture of the initial metallic material and the dispersoid, prior to the step of consolidating. Such mechanical deforma-

tion is unnecessary with the present approach, unlike the mechanical alloying approach.

[0036] Figure 4 illustrates the microstructure of the metallic article 70 having a surface 72 facing the environment 74. The metallic article 70 has a microstructure of an alloy matrix 76 with unreacted stable-dispersoid-forming additive element(s) and/or the dispersoids dispersed generally uniformly therethrough. The stable-dispersoid-forming additive element(s) may be present in solid solution, numeral 78, or as one or more unreacted discrete phases 80. (If the dispersoids are added in their final form, there will be little or none of the unreacted element in solid solution 78 or the unreacted discrete phases 80.) Some of the stable-dispersoid-forming additive element(s) initially in solid solution may have been furnished as, or reacted with oxygen initially present in the matrix 76 to form, a dispersion of fine stable dispersoids 82. Some of the stable-dispersoid-forming additive element(s) initially present as unreacted discrete phase 80 may have been furnished as, or reacted with oxygen initially present in the matrix 76 to form, a dispersion of coarse stable dispersoids 84. (As used herein, "coarse" and "fine" are used only in a relative sense to each other, with "coarse" dispersoids being larger in size than "fine" dispersoids. Both the coarse stable dispersoids and the fine stable dispersoids provide strengthening effects.) These stable dispersoids 82 and 84 are distributed substantially uniformly throughout the matrix 76.

[0037] The primary embodiment of the present approach is therefore directed to the formation of a substantially uniform distribution of dispersoids 38 in the matrix 34. The uniformity is microscopically judged quantitatively at a depth of more than about 0.003 inches from the surface, in a square field of about 0.008 inches on a side. Mean spacings of the particles are measured in this field, and compared with values in other fields at depths of more than about 0.003 inches from the surface, measured separately but in the same manner. Desirably, the mean spacings of the particles are within about 25 percent, more preferably about 10 percent, of each other in the different fields.

[0038] Optionally but typically, there is further processing, step 56, of the consolidated article. In this processing, the article is not melted. Such further processing may include, for example, mechanically forming the consolidated article by any operable approach, machining the consolidated article by any operable approach, coating the consolidated article by any operable approach, or heat treating the consolidated article by any operable approach. These steps are selected according to the type of matrix and dispersoid, the shape required, and the application. Such procedures are known generally in the art.

[0039] In addition to the bulk-alloy improvements, some near-surface modification of the metallic alloy is possible, in some alloy systems and for some dispersoids. The result is a non-uniform distribution of disper-

soids, in the near-surface region. In one type of further processing 56 that produces such a non-uniform distribution of dispersoids, the consolidated metallic article is exposed to an oxygen-containing environment at a temperature greater than room temperature, and preferably greater than about 500°F. If there is unreacted stable-dispersoid-forming element 78 or 80 present in the material, the oxygen exposure, leading to the types of non-uniform microstructure shown in Figure 5, may be either during the initial preparation of the metallic article, in a controlled production setting, or during later service exposure at elevated temperature. In any of these cases, the oxygen diffuses inwardly from the surface 72 into the matrix 76. The inwardly diffused oxygen chemically reacts with the stable-dispersoid-forming additive element(s) that are present near the surface 72 either in solid solution 78 or in discrete phases 80. The result is that few if any unreacted stable-dispersoid-forming additive elements in solid solution 78 or in discrete phases 80 remain near the surface 72, and instead are all reacted to form, respectively, additional fine stable dispersoids 82 and coarse stable dispersoids 84. Consequently, there is a higher concentration of fine stable dispersoids 82 in a diffusion-oxidation zone 86 of depth D1 at and just below the surface 72, as compared with the concentration of the fine stable dispersoids 82 at greater depths. D1 is typically in the range of from about 0.001 to about 0.003 inches for titanium alloys, but may be smaller or larger.

[0040] In some circumstances the stable dispersoids 82 and 84 have a higher specific volume than the stable-dispersoid-forming additive elements from which they are produced. This higher specific volume creates a compressive force, indicated by arrow 90, in the matrix 76 near the surface 72. The compressive force 90 inhibits crack formation and growth when the article is loaded in tension or torsion during service, a highly beneficial result. Additionally, depending upon the specific dispersoid formed by the stable-dispersoid-forming elements, there may be formed a stable surface layer 88, that may serve as a diffusion barrier to the diffusion of oxygen and other elements from the environment 74 into the article 40. Although this non-uniform dispersoid structure is discussed in terms of the most-preferred case, inward diffusion from the free surface 72 of the dispersion-forming element oxygen, the same principles apply to inward diffusion of other dispersoid-forming elements such as nitrogen, carbon, silicon, sulfur, boron, and other dispersion-forming elements that are combinable with the metallic elements in the matrix to form the dispersoid. The dispersion-forming element is preferably supplied from a gaseous phase that contains the dispersion-forming element in either combined or uncombined form, but it may also be provided in some cases from a solid or liquid contacting the free surface 72.

[0041] This structure is to be distinguished from that shown in Figure 6, a conventional titanium alloy article 100 that is outside the scope of the present approach.

In this case, during exposure to an oxygen-containing environment during processing and/or service, oxygen diffuses from the environment 74, through the surface 72, and into the base metal of the article 100 to a depth D2, which is typically from about 0.003 to about 0.005 inch in titanium alloys. In the instance of certain titanium alloys, for example, the excess oxygen reacts with and embrittles the alpha-phase titanium in this region to form an alpha case 102. In the present approach as illustrated in Figure 5, on the other hand, the gettering of the inwardly diffusing oxygen by the stable-dispersoid-forming additive elements and the stable surface layer 88 combined to reduce and, desirably, avoid the formation of such an oxygen-stabilized alpha case.

[0042] The presence and the nature of the distribution of the stable dispersoids 82 and 84, in either a uniform or non-uniform distribution, has several additional important consequences. The stable dispersoids 82 and 84 serve to stiffen the matrix 76 by the composite-stiffening effect, strengthen the matrix 76 by the dispersion-strengthening effect and/or the composite strengthening effect, and also improve the elevated-temperature creep strength of the matrix 76. The stable dispersoids 82 and 84 may also pin grain boundaries of the matrix 76 to inhibit coarsening of the grain structure.

[0043] When the dispersoid precursor approach is used and the dispersoid precursor is a preferential oxygen getter, the dispersoids 38, 82, 84 in the metallic matrix 34, 76 also remove oxygen (or other combinable element such as nitrogen, carbon, boron, or sulfur) from the matrix 34, 76, regardless of how the oxygen (or other combinable element) was introduced into the matrix 34, 76. Desirably, substantially all of the oxygen (or other combinable element) is removed from solid solution. Too much oxygen (or other element) in solid solution in the matrix 34, 76 may have adverse effects on the properties of the initial metallic material and/or the consolidated article in some cases. Removal of at least a portion of, and in some cases substantially all of, the oxygen (or other combinable element) may also allow other desirable alloying elements to be introduced into the matrix to a degree greater than possible when a substantial oxygen (or other combinable element) content is present in solid solution.

[0044] The present approach may be used to prepare a wide range of dispersion-strengthened alloys, including without limitation nickel-base, iron-base, cobalt-base, and aluminum-base alloys. These dispersion-strengthened alloys include alloys similar in composition to those which can be produced by other techniques such as mechanical alloying (but having the advantages over mechanical alloying discussed herein, and alloys that cannot be prepared in dispersion-strengthened form by other approaches. Some specific examples include nickel-base alloys such as MA754, dispersion-strengthened Rene™108, dispersion-strengthened Rene™125, and dispersion-strengthened Alloy 718; iron-base alloys such as MA956 and dispersion-

strengthened A286; titanium-base alloys such as dispersion-strengthened Ti-6242; cobalt-base alloys such as dispersion-strengthened L605; and aluminum-base alloys such as Al-9052, and Al-905XL; and dispersion strengthened 7075. The present approach is not limited to these alloys, which are presented as examples and not by way of limitation.

[0045] For completeness, various aspects of the invention are set out in the following numbered clauses:

1. A method of preparing an article (20) comprising a metallic matrix (34) having its constituent elements and a dispersoid (38) distributed therein, comprising the steps of:

furnishing at least one nonmetallic matrix precursor compound, all of the nonmetallic matrix precursor compounds collectively including the constituent elements of the metallic matrix (34) in their respective constituent element proportions; thereafter producing a mixture of an initial metallic material and the dispersoid (38), the step of producing including the step of:

chemically reducing the matrix precursor compounds to produce the initial metallic material, without melting the initial metallic material; and consolidating the mixture of the initial metallic material and the dispersoid (38) to produce a consolidated article (20) having the dispersoid (38) distributed in the metallic matrix (34) comprising the initial metallic material, without melting the initial metallic material, without melting the dispersoid (38), and without melting the consolidated article (20).

2. The method of clause 1, wherein the step of producing includes the steps of:

furnishing the dispersoid (38), and mixing the dispersoid (38) with the matrix precursor compounds prior to or concurrently with the step of chemically reducing.

3. The method of clause 1, wherein the step of producing includes the steps of:

furnishing the dispersoid (38), and mixing the dispersoid (38) with the initial metallic material after the step of chemically reducing.

4. The method of clause 1, wherein the step of producing includes the steps of:

- furnishing a dispersoid-precursor, and mixing the dispersoid precursor with the matrix precursor compound prior to or concurrently with the step of chemically reducing, and wherein the dispersoid precursor chemically reacts during the step of chemically reacting to produce the dispersoid (38).
- 5 The method of clause 1, wherein the step of producing includes the steps of:
- 10 first chemically reducing the matrix precursor compounds to produce the initial metallic material, without melting the initial metallic material,
- 15 introducing a precursor compound of the dispersoid (38) into the initial metallic material, second chemically reducing the precursor compound of the dispersoid (38) to produce a first element of the dispersoid (38), and
- 20 chemically reacting the first element of the dispersoid (38) with a second element of the dispersoid (38).
- 25 The method of clause 1, wherein there is no mechanical deformation of the initial metallic material prior to the step of consolidating.
- 30 The method of clause 1, wherein the step of furnishing at least one nonmetallic matrix precursor compound includes the step of:
- 35 furnishing a compressed mass of the matrix precursor compounds.
- 40 The method of clause 1, wherein the step of furnishing at least one nonmetallic matrix precursor compound includes the step of:
- 45 furnishing a compressed mass of nonmetallic matrix precursor compounds larger in dimensions than those of the consolidated article (20).
- 50 The method of clause 1, wherein the step of chemically reducing includes the step of:
- 55 producing a sponge of the initial metallic material.
- 60 The method of clause 1, wherein the step of chemically reducing includes the step of:
- 65 producing particles of the initial metallic material.
- 70 The method of clause 1, wherein the step of chemically reducing includes the step of:
- 75 chemically reducing the mixture of nonmetallic matrix precursor compounds by solid-phase reduction.
- 80 The method of clause 1, wherein the step of chemically reducing includes the step of:
- 85 chemically reducing the compound mixture by vapor-phase reduction.
- 90 The method of clause 1, wherein the step of consolidating includes the step of:
- 95 consolidating the initial metallic material using a technique selected from the group consisting of hot isostatic pressing, forging, pressing and sintering, and containerized extrusion.
- 100 The method of clause 1, including an additional step, after the step of consolidating, of:
- 105 forming the consolidated article (20).
- 110 The method of clause 1, including an additional step, after the step of chemically reducing, of:
- 115 heat treating the consolidated article (20).
- 120 The method of clause 1, wherein the step of producing includes the step of:
- 125 producing the initial metallic material selected from the group consisting of a nickel-base material, an iron-base material, a cobalt-base material, a titanium-base material, a magnesium-base material, and an aluminum-base material.
- 130 The method of clause 1, wherein the step of producing the mixture includes the step of:
- 135 producing a dispersoid (38) including an element selected from the group consisting of oxygen, carbon, nitrogen, boron, sulfur, and combinations thereof.
- 140 The method of clause 1, including an additional step, of:
- 145 exposing, at a temperature greater than room temperature, the consolidated article (20) to an environment containing a dispersion-forming element.

## Claims

1. A method of preparing an article (20) comprising a metallic matrix (34) having its constituent elements



and a dispersoid (38) distributed therein, comprising the steps of:

furnishing at least one nonmetallic matrix precursor compound, all of the nonmetallic matrix precursor compounds collectively including the constituent elements of the metallic matrix (34) in their respective constituent-element proportions; thereafter producing a mixture of an initial metallic material and the dispersoid (38), the step of producing including the step of:

chemically reducing the matrix precursor compounds to produce the initial metallic material, without melting the initial metallic material; and consolidating the mixture of the initial metallic material and the dispersoid (38) to produce a consolidated article (20) having the dispersoid (38) distributed in the metallic matrix (34) comprising the initial metallic material, without melting the initial metallic material, without melting the dispersoid (38), and without melting the consolidated article (20).

2. The method of claim 1, wherein the step of producing includes the steps of:

furnishing the dispersoid (38), and mixing the dispersoid (38) with the matrix precursor compounds prior to or concurrently with the step of chemically reducing.

3. The method of claim 1, wherein the step of producing includes the steps of:

furnishing the dispersoid (38), and mixing the dispersoid (38) with the initial metallic material after the step of chemically reducing.

4. The method of claim 1, wherein the step of producing includes the steps of:

furnishing a dispersoid-precursor, and mixing the dispersoid precursor with the matrix precursor compound prior to or concurrently with the step of chemically reducing, and wherein the dispersoid precursor chemically reacts during the step of chemically reacting to produce the dispersoid (38).

5. The method of claim 1, wherein the step of producing includes the steps of:

first chemically reducing the matrix precursor

compounds to produce the initial metallic material, without melting the initial metallic material,

introducing a precursor compound of the dispersoid (38) into the initial metallic material, second chemically reducing the precursor compound of the dispersoid (38) to produce a first element of the dispersoid (38), and chemically reacting the first element of the dispersoid (38) with a second element of the dispersoid (38).

6. The method of claim 1, wherein the step of furnishing at least one nonmetallic matrix precursor compound includes the step of:

furnishing a compressed mass of the matrix precursor compounds.

7. The method of claim 1, wherein the step of chemically reducing includes the step of:

producing particles of the initial metallic material.

8. The method of claim 1, wherein the step of chemically reducing includes the step of:

chemically reducing the mixture of nonmetallic matrix precursor compounds by solid-phase reduction.

9. The method of claim 1, wherein the step of chemically reducing includes the step of:

chemically reducing the compound mixture by vapor-phase reduction.

10. The method of claim 1, including an additional step, after the step of chemically reducing, of:

heat treating the consolidated article (20).

FIG. 1

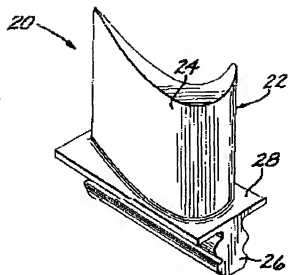
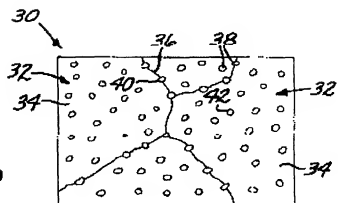


FIG. 2



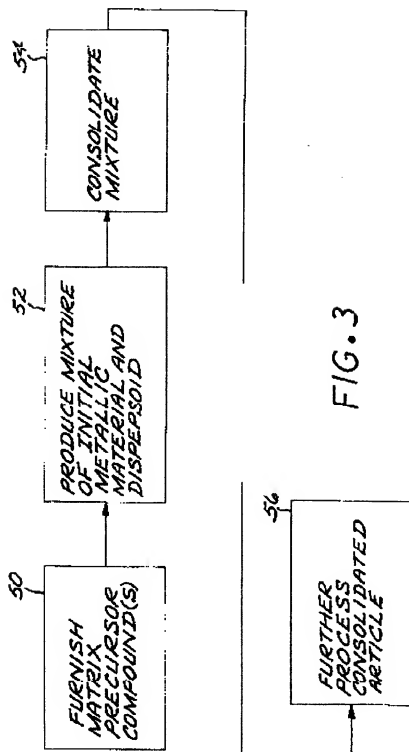
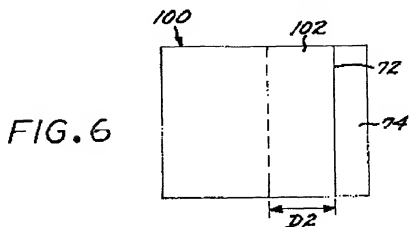
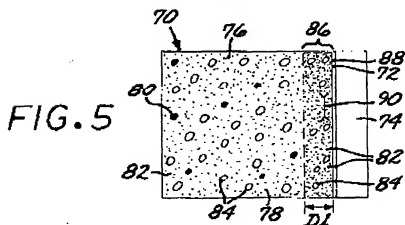
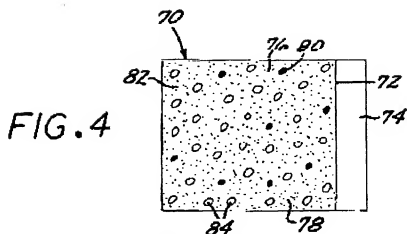


FIG. 3





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(54) Article having a dispersion of ultrafine titanium boride particles in a titanium-base matrix

(57) An article (20) includes a microscale composite material (21) having a matrix (22) with more titanium than any other element, and a dispersion of titanium boride

particles (24, 25) in the matrix (22). At least about 50 volume percent of the titanium boride particles (24, 25) have a maximum dimension of less than about 2 micrometers.

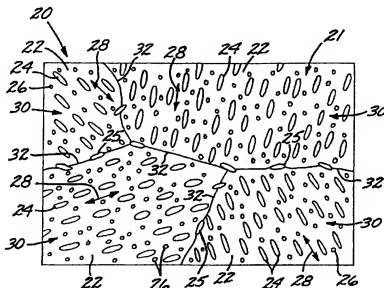


FIG. 1

EP 1 657 317 A1

## Description

[0001] This invention relates to articles having titanium-base metallic compositions and, more particularly, to articles made of titanium-base compositions having titanium boride particles dispersed therein.

[0002] One of the most demanding applications of materials in aircraft gas turbine engines is compressor and fan disks (sometimes termed "rotors") upon which the respective compressor blades and fan blades are supported. The disks rotate at many thousands of revolutions per minute, in a moderately elevated-temperature environment, when the gas turbine is operating. They must exhibit the required mechanical properties under these operating conditions.

[0003] Some of the gas turbine engine components, such as some of the compressor and fan disks, are fabricated from titanium metallic compositions. The disks are typically manufactured by furnishing the metallic constituents of the selected titanium metallic composition, melting the constituents, and casting an ingot of the titanium metallic composition. The cast ingot is then converted into a billet. The billet is further mechanically worked, typically by forging. The worked billet is thereafter upset forged, and then machined to produce the titanium-base metallic composition component.

[0004] Achieving the required mechanical properties at room temperature and up to moderately elevated temperatures, retaining sufficient environmental resistance, and preventing premature failure offer major challenges in the selection of the materials of construction and the fabrication of the articles. The chemistry and microstructure of the metallic composition must ensure that the mechanical properties of the article are met over the service temperature range of at least up to about 1200°F for current titanium-base metallic composition components. The upper limit of about 1200°F for service of such components is due principally to static-strength and creep-strength reduction at higher temperatures and the tendency for titanium to react with oxygen at elevated temperatures, forming a brittle oxygen-enriched layer, termed alpha case. Small mechanical or chemical irregularities in the final component may cause it to fail prematurely in service, and these irregularities must be minimized or, if present, be detectable by available inspection techniques and taken into account. Such irregularities may include, for example, mechanical irregularities such as cracks and voids, and chemical irregularities such as hard alpha irregularities (sometimes termed low-density inclusions) and high-density inclusions.

[0005] One recent approach to improving the properties of titanium-base metallic compositions, including the high-temperature strength, is the introduction of boron into the metallic composition to produce titanium boride particles dispersed therein. The introduction of boron has been accomplished by several different methods, such as conventional cast-and-wrought processing, powder metallurgy techniques such as gas atomization, and a

blended elemental approach. The first two methods suffer from the limited solubility of boron in titanium. The boron tends to segregate strongly, forming relatively large titanium boride particles that are detrimental to ductility and fatigue. In order to avoid the segregation problem, the levels of boron added to the metallic composition by these first two methods is severely restricted, usually to the hypoeutectic portion of the phase diagram, limiting the potential benefits of the boron addition, or the cooling rate during solidification must be very high. The blended elemental approach allows much larger additions of boron. However, because the boron is typically added as titanium diboride, and the phase in thermodynamic equilibrium with the alpha phase of titanium is the very-stable titanium monoboride, extended times at elevated temperatures are required to fully convert the titanium diboride to titanium monoboride. The required high temperatures and long times prevent the production of a uniform fine dispersion of titanium boride particles in the metallic composition. Additionally, fine freestanding titanium boride or titanium diboride particles tend to agglomerate, reducing the uniformity of the final product. The result of all of these production approaches is that a significant volume fraction of the titanium boride is present as large particles that are typically 10-100 micrometers in their largest dimensions. These large particles have some beneficial strengthening effects, but they are not optimal for ductility, crack initiation, and static, creep, and fatigue strength.

[0006] It has been possible, using existing melting, casting, and conversion practice, to prepare non-boron-containing titanium-base metallic composition components such as compressor and fan disks that are fully serviceable. However, there is a desire and need for a manufacturing process to produce the disks and other components with even further-improved properties arising from the presence of titanium boride particles and greater freedom from irregularities, thereby improving the operating margins of safety. The present invention fulfills this need for an improved process, and further provides related advantages.

[0007] The present invention provides a metallic article of a titanium-base composition that also contains boron in an amount greater than the solubility limit of the boron in the metallic composition. The intragranular titanium boride particles distributed in the titanium matrix are small in size, typically well below 1 micrometer in their largest dimensions. The article has a good combination of mechanical properties in the temperature range up to about 1300°F, possible good resistance to environmental damage from oxidation, and a low incidence of irregularities. The elastic modulus of the material is improved and the wear resistance is increased by the presence of the titanium boride particles. The boride dispersion is more uniform and finer than that resulting from other production techniques. The material produced by the present approach has better static and creep strength at the same operating temperatures as compared with conventional

titanium metallic compositions, and also allows the material to be used to higher operating temperatures than possible with conventional titanium metallic compositions.

[0008] An article comprises a microscale composite material having a matrix comprising more titanium by weight than any other element, and a dispersion of titanium boride particles in the matrix. At least about 50 volume percent, more preferably at least about 90 volume percent, and most preferably at least about 99 volume percent, of the intragranular titanium boride particles have a maximum dimension of less than about 2 micrometers. More preferably, at least about 50 volume percent, more preferably at least about 90 volume percent, and most preferably at least about 99 volume percent, of the intragranular titanium boride particles have a maximum dimension of less than about 1 micrometer. More preferably, at least about 50 volume percent, more preferably at least about 90 volume percent, and most preferably at least about 99 volume percent, of the intragranular titanium boride particles have a maximum dimension of less than about 0.5 micrometer. Even more preferably, at least about 50 volume percent, more preferably at least about 90 volume percent, and most preferably at least about 99 volume percent, of the intragranular titanium boride particles have a maximum dimension of less than about 0.2 micrometer.

[0009] As used herein in describing the present approach, "titanium boride" refers to  $TiB$ ,  $TiB_2$ ,  $Ti_2B_3$ , or other titanium-boron-containing compounds, whose composition may be modified by alloying elements. "Titanium-base" includes pure titanium, metallic alloys of titanium and other elements, and titanium-base intermetallic alloys, as long as there is more titanium by weight than any other element. The "matrix" is the metallic titanium-base material in which the titanium boride particles are distributed and dispersed.

[0010] The boron constituent element is preferably present in an amount not greater than that required to form about 90 percent by volume titanium boride in the consolidated material. More preferably, the boron is present in the consolidated material in an amount of not greater than about 17 weight percent of the consolidated material. Even more preferably, the boron is present in the consolidated material in an amount of from about 0.05 to about 17 weight percent of the consolidated material.

[0011] The amount of boron present in the material may be considered in two ranges, a hypoeutectic range, which for the titanium-boron binary system is from about 0.05 to about 1.5 percent by weight boron, and a hyper-eutectic range, which for the titanium-boron binary system is from about 1.5 to about 17 percent by weight boron. Alloys with other elements in addition to titanium and boron may have other phases and ranges, but are within the scope of the present approach. The present approach permits the preparation of materials having the same boron content as may be achieved with other techniques,

typically up to about 5 percent by weight of boron, and also the preparation of materials having greater boron content than may be readily achieved with other techniques, typically in the range of from about 5 to about 17 percent by weight of boron. In each case, the materials made by the present approach typically have a fine, uniform titanium boride dispersion.

[0012] As stated, boron is preferably present at a level in excess of its room-temperature solid solubility in the titanium-base composition matrix, up to the level required to form no more than about 90 percent by volume titanium boride. For smaller additions in excess of the limit of solid solubility, the fine dispersion of titanium boride particles provides significant high-temperature static strength and high-temperature creep strength benefits by fine-particle strengthening. For larger additions in excess of the limit of solid solubility, there is a larger volume fraction of fine titanium boride particles present and substantial rule-of-mixtures-strengthening benefits in addition to the fine-particle strengthening. At both levels of boron additions in excess of the solid solubility limit, the strength, elastic modulus, and wear resistance of the material are significantly improved over conventional titanium-base compositions.

[0013] The matrix is typically polycrystalline, preferably has a grain size of less than about 10 micrometers and more preferably less than about 5 micrometers. The titanium boride particles are preferably formed in situ within the matrix, so that they are never freestanding, freely flowing particles during the preparation of the microscale composite material. The intragranular (i.e., those not at the grain boundaries) titanium boride particles are preferably crystallographically oriented relative to the matrix within each grain, and more preferably are coherent or partially coherent with the matrix within each grain.

[0014] The microscale composite material is desirably mechanically within 20 percent of isotropic, more preferably within 10 percent of isotropic. That is, the article may be made by the preferred method so that the mechanical properties may be nearly the same measured in all directions. This state is to be contrasted with the anisotropic mechanical properties usually observed for other titanium-titanium boride materials, in which the rodlike titanium boride particles are aligned with a mechanical working direction, such as the major axis of an extrusion, producing mechanical strength properties that are significantly greater in the working direction than in directions transverse to the working direction. On the other hand, the properties of the present articles may be made anisotropic if desired.

[0015] The intragranular titanium boride particles of the present approach are preferably plate-like in shape. That is, two dimensions, defining a face of the plate, are relatively large (but not necessarily the same) and one dimension, defining a thickness of the plate, is relatively small. However, the intragranular titanium boride particles need not be plate-like, but may instead be equiaxed,

rodlike (with one relatively large dimension and two relatively small dimensions), or of another shape.

[0016] There may optionally be present an oxide of a stable-oxide-forming additive elements include magnesium, calcium, scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium, and mixtures thereof.

[0017] The material thus is a titanium-base matrix containing a fine dispersion of titanium boride particles, and optionally with stable-oxide-forming additive element(s) dispersed therethrough. The optional stable-oxide-forming additive element or elements are present in solid solution (either below the solubility limit or in a supersaturated state) and/or as one or more discrete dispersed oxide phases. The dispersed phases may be unoxidized stable-oxide-forming additive elements or an already oxidized dispersion or a mixture of both. The stable-oxide-forming additive elements that are in solid solution or a non-oxidized discrete dispersion are available for subsequent reaction with oxygen that may be in the matrix or diffuses into the metallic material in subsequent processing or service.

[0018] The microscale composite material may form the entire article, or may be present as a microscopic or macroscopic insert to another article that is manufactured via any route, including traditional casting and working, casting, or similar approach as described herein. In any of these embodiments where the microscale composite material is added as an insert, the surrounding article may have the same or a different composition.

[0019] The formation of the boride dispersion has several important benefits. First, a substantially uniformly distributed fine dispersion aids in achieving the desired mechanical properties, including static strength, fatigue strength, and creep strength, which are stable over extended periods of exposure at elevated temperatures, through dispersion strengthening of the titanium-base matrix. The substantially uniformly distributed dispersion also aids in limiting grain growth of the titanium-base matrix. Second, the modulus of elasticity of the titanium-base composition is significantly increased, allowing the article to withstand substantially higher loads while deforming elastically. Third, the wear resistance and erosion resistance of the article are substantially improved, allowing increased service time in a given application. Fourth, the presence of the fine dispersion results in improved ductility compared with an article prepared by a conventional cast-and-wrought, cast, or gas-atomized or blended-elemental powder metallurgy approach. The boride dispersion may be formed in any titanium-base composition matrix, including alpha, near-alpha, alpha-plus-beta, near-beta, and beta titanium metallic compositions, and any titanium-base intermetallics including those based on the alpha-2, orthorhombic, and gamma titanium aluminides.

[0020] The optional oxide dispersion has several im-

portant benefits. First, a substantially uniformly distributed dispersion aids in achieving the desired mechanical properties, which are stable over extended periods of exposure at elevated temperature, through further dispersion strengthening of the base-metal matrix, and also aids in limiting grain growth of the base-metal matrix. Second, when the exposure to environmental oxygen occurs during a pre-service oxidation or during service, the oxygen diffusing into the article would normally cause the formation of an "alpha case" near the surface of conventional alpha-phase-containing titanium metallic compositions. In the present approach, the stable-oxide-forming additive elements either in solution or as a separate phase getter the inwardly diffusing oxygen from solid solution and adding to the oxide dispersion, thereby reducing the incidence of alpha case formation and the associated surface embrittlement and possible premature failure. Third, in some cases the oxide dispersoids have a greater volume than the discrete metallic phases from which they were formed. The formation of the oxide dispersoids produces a compressive stress state that is greater near to the surface of the article than deeper in the article. The compressive stress state aids in preventing premature crack formation and growth during service. Fourth, the formation of a stable oxide dispersion at the surface of the article acts as a barrier to the inward diffusion of additional oxygen. Fifth, the removing of excess oxygen in solution from the matrix allows the introduction of higher metallic alloying levels of alpha-stabilizer elements such as aluminum and tin, in turn promoting improved modulus of elasticity, creep strength, and oxidation resistance of the matrix. Sixth, the presence of excess oxygen in solution in some types of titanium metallic compositions, such as alpha-2, orthorhombic, and gamma-based aluminides, reduces the ductility of the titanium metallic composition. The present approach getters that oxygen, so that the ductility is not adversely affected. [0021] A preferred method for producing such an article made of constituent elements in constituent-element proportions includes the steps of furnishing at least one nonmetallic precursor or compound, wherein all of the non-metallic precursor compounds collectively contain the constituent elements in their respective constituent-element proportions. The constituent elements comprise a titanium-base composition, and boron present at a level greater than its room-temperature solid solubility limit in the titanium-base composition. The precursor compounds are chemically reduced to produce a material comprising a titanium-base composition having titanium boride particles therein, without melting the titanium-base composition that forms the matrix. The titanium-base composition does not have a melted microstructure, but instead is more uniform and without the segregation features associated with melting and solidifying. The titanium-base composition having the titanium boride particles therein is consolidated to produce a consolidated article, without melting the titanium-base composition and without melting the consolidated titanium-base com-



position. The absence of melting aids in achieving and maintaining the fine size distribution of the titanium boride particles. The various steps of this processing are preferably performed at as low a temperature as possible in each case, to avoid coarsening the titanium boride particles and the optional oxide dispersion and/or strong-oxide-former particles. The present approach is compatible with the embodiments discussed herein and those incorporated by reference.

[0022] Optionally, the step of furnishing may include the step of furnishing a nonmetallic precursor compound of a stable-oxide-forming additive element that forms a stable oxide in the titanium-base composition. In such a material, at least one additive element is present at a level greater than its room-temperature solid solubility limit in the titanium-base composition. The preferred method includes an additional step, after the step of chemically reducing, of oxidizing the metallic composition, including the oxygen-forming additive element, at a temperature greater than room temperature.

[0023] The consolidated article may be mechanically formed as desired, by any mechanical forming technique.

[0024] The material may be heat treated either after the chemical reduction step, after the consolidation step (if used), after mechanical forming, or subsequently.

[0025] The steps of the preferred approach, the chemical reduction and consolidating steps as well as any other processing steps, are performed at temperatures below the melting point of the matrix and the titanium boride particles, and preferably at as low an elevated temperature as possible and for as short a time as possible at the elevated temperature. The higher the temperature and the longer the time, the coarser will be the titanium boride particles and the optional oxide particles. Process steps are chosen with this limitation in mind. For example, vapor phase chemical reduction is preferred to solid phase chemical reduction, because the vapor phase chemical reduction is typically performed at a lower temperature and/or for a shorter time than is solid phase chemical reduction. Consolidation techniques such as extrusion are preferred to pressing and sintering for the same reason.

[0026] The present approach thus provides a titanium-base article having a fine titanium boride dispersion therein, with improved properties and improved stability. Other features and advantages of the present invention will be apparent from the following more detailed description of the preferred embodiment, taken in conjunction with the accompanying drawings, which illustrate, by way of example, the principles of the invention, and in which:

Figure 1 is an idealized microstructure of the metallic article;

Figure 2 is a schematic perspective view of a titanium boride particle;

Figure 3 is a perspective view of a gas turbine com-

ponent made by the present approach and having a titanium-boron insert;

Figure 4 is a sectional view of the gas turbine component of Figure 3, taken on line 4-4;

Figure 5 is a block flow diagram of an approach for practicing the invention;

Figures 6-8 are idealized comparative microstructures illustrating the relative size of titanium boride particles compared to a grid representing the grain size of the matrix, wherein Figure 6 represents the microstructure for material produced by a gas atomized approach, Figure 7 represents the microstructure for material produced by a blended elemental approach, and Figure 8 represents the microstructure for material produced by the present approach.

[0027] Figure 1 is an idealized microstructure of an article 20 including a microscale composite 21 formed of a polycrystalline titanium-base matrix 22 having a dispersion of fine platelike intragranular titanium boride particles 24 and grain-boundary titanium boride particles 25 therein. Optionally, there are oxide particles 26 dispersed in the matrix 22 as well. In Figure 1, the oxide particles 26 are illustrated as smaller in size than the titanium boride particles 24 and 25. However, the oxide particles 26 may be of comparable size with the titanium boride particles 24 and 25, or of larger size than the titanium boride particles 24 and 25. (This idealized microstructure of Figure 1 does not reflect the relative sizes or volume fractions of the constituents.)

[0028] The constituent elements comprise a titanium-base composition, boron, and optionally a stable-oxide-forming additive element. A titanium-base composition has more titanium by weight than any other element (although there may not be more titanium by atomic fraction than any other element, as for example in some gamma-phase titanium aluminides). The titanium-base matrix 22 may be pure titanium (e.g., commercially pure or CP titanium), a metallic alloy of titanium and other elements, or a titanium-base intermetallic alloy. Titanium metallic alloy compositions of particular interest include alpha-beta phase titanium metallic compositions, beta-phase titanium metallic compositions, alpha-2 phase, and orthorhombic phase. A titanium-base intermetallic alloy of particular interest is the gamma-phase titanium aluminide metallic composition. The matrix composition is not limited to these compositions, however.

[0029] The matrix 22 is polycrystalline, with portions of four differently oriented grains 30 illustrated, separated by grain boundaries 32. ("Grains" are also sometimes termed "crystals".) The grain size of the grains 30 is preferably less than 10 micrometers, more preferably less than 5 micrometers. The matrix 22 within each of the grains 30 has a crystallographic orientation, represented schematically by arrow 28. The intragranular titanium bo-

ride dispersoid particles 24 (i.e., those titanium boride dispersoid particles which are not at the grain boundaries) are preferably crystallographically oriented relative to the crystallographic orientation 28 of the matrix 22 within each grain 30. More preferably, the intragranular titanium boride particles 24 are coherent or partially coherent with the matrix 22 within each grain 30. A coherent interface occurs when lattice planes crossing the interface are continuous, although possibly change orientations. A semi-coherent or partially coherent interface is closely analogous to a low angle boundary in that uniform misfit is related into regions of good, coherent fit separated by regions of bad fit, i.e., dislocations. Coherency is completely lost when the misfit is so large that the interface dislocation spacing is approximately the lattice spacing. The noncoherent interphase boundary is therefore analogous to the high angle grain boundary and occurs when there is no simple fit between the lattices of the two phases. The grain-boundary titanium boride particles 25 are distinct from the intragranular titanium boride particles 24 in respect to preferred orientation, since the orientations of the grain-boundary titanium boride particles 25 may be influenced by the adjoining grains, grain boundary dislocation structures, and the like.

[0030] The presence of the preferential orientation of the intragranular titanium boride dispersoid particles 24 relative to the crystallographic direction 28 of the matrix 22 is to be distinguished from the situation found in relation to titanium-titanium boride materials made by other approaches. In the other approaches, the titanium boride particles are typically oriented relative to the working direction, such as a rolling direction or an extrusion direction, rather than in relation to the crystallographic orientation of the matrix. The result is that the mechanical properties of these other materials are typically highly anisotropic after working, with the highest modulus and strength, and lowest ductility, measured parallel to the orientation direction of the titanium boride particles. The present approach leads to a greater degree of isotropy of the titanium boride particles, due to the more nearly random crystallographic orientations of the various grains, when averaged over the entire microscale composite material, and hence the more nearly random orientations of the particles, when averaged over the entire microscale composite material. Desirably, at least one of the mechanical properties of the microscale composite material of the titanium boride particles 24, 25 in the titanium matrix 22 is within 20 percent of isotropic, meaning that its measured values for all measurement directions are within 20 percent of a value averaged over all measurement directions. Preferably, at least one of the mechanical properties of the microscale composite material is within 10 percent of isotropic. However, the properties of the microscale composite material may be made more anisotropic, if desired, by processing treatments such as thermal processing and/or mechanical working.

[0031] The boron level ranges from greater than the solubility limit at room temperature of boron in the titani-

um-base composition to the level required to produce no more than 90 percent by volume titanium boride. Typically, the boron is present in an amount of from 0.05 percent to 17 percent by weight of the total weight of the final consolidated material. The result is a material having at least two phases, including one or more metallic phases constituting the titanium-base matrix 22, the titanium boride particles 24 and 25, and optionally one or more types of stable oxide particles 26. As used herein in describing the present method, "titanium boride" refers to TiB, which is present in most materials made by the present approach, TiB<sub>2</sub>, which is present where the matrix is a gamma-phase titanium aluminide, Ti<sub>3</sub>Al<sub>4</sub>, and/or other titanium borides or other titanium-boron-containing compounds, possibly modified due to the presence of alloying elements. "Titanium monoboride" refers specifically to TiB, and "titanium diboride" refers specifically to TiB<sub>2</sub>.

[0032] It is most preferred that the amount of boron is not less than that required to produce a volume fraction of at least 0.25 volume percent, more preferably at least 0.75 volume percent, even more preferably at least 2 volume percent of titanium boride particles in the matrix. 0.25 volume percent is the amount of 10 nanometer titanium boride particles estimated to yield an increase of 20,000 pounds per square inch in the shear strength of the material; 0.75 volume percent is the amount of 20 nanometer titanium boride particles estimated to yield an increase of 20,000 pounds per square inch in the shear strength of the material; and 2 volume percent is the amount of 30 nanometer titanium boride particles estimated to yield an increase of 30,000 pounds per square inch in the yield strength of the material.

[0033] The fine intragranular titanium boride dispersoid particles 24 provides dispersoid (i.e., Crowan) strengthening by interacting with dislocations in the titanium-base composition matrix 22. These fine intragranular dispersoid particles 24 are smaller in size than those produced by prior processes for preparing titanium-titanium boride materials. Figures 6-8 are idealized comparative microstructures illustrating the relative size of titanium boride particles 70 compared to a grid 72 representing the grain size of the matrix by two prior approaches (Figure 6, for a gas atomized approach and Figure 7 for a blended elemental approach), with the present approach (Figure 8). With an increasing amount of boron present, the volume fraction of titanium boride increases so that it becomes more nearly continuous at a macroscopic level, but still maintains a separate distribution of fine, less than 1 micrometer, titanium boride on a microscopic level.

[0034] Figure 2 shows in isolation a single intragranular titanium boride dispersoid particle 24 at an even higher magnification than shown in Figure 1. The intragranular particle 24 typically has a plate-like shape, with two relatively large dimensions that define the face of the plate and a relatively small dimension that defines the thickness of the plate. The maximum dimension L of one of

the two relatively large dimensions of the face of the plate is the maximum dimension of the intragranular titanium boride dispersoid phase particle 24.

[0035] In the present approach, at least 50 volume percent, more preferably at least 90 volume percent, and most preferably at least 99 volume percent, of the intragranular titanium boride particles 24 have a maximum dimension L of less than 2 micrometers. More preferably, at least 50 volume percent, more preferably at least 90 volume percent, and most preferably at least 99 volume percent, of the intragranular titanium boride particles 24 have a maximum dimension L of less than 1 micrometer. More preferably, at least 50 volume percent, more preferably at least 90 volume percent, and most preferably at least 99 volume percent, of the intragranular titanium boride particles 24 have a maximum dimension L of less than 0.5 micrometer. Even more preferably, at least 50 volume percent, more preferably at least 90 volume percent, and most preferably at least 99 volume percent, of the intragranular titanium boride particles 24 have a maximum dimension L of less than 0.2 micrometer.

[0036] The optional oxide particles 26 are formed by the reaction of oxygen with one or more stable-oxide-forming additive elements. An element is considered to be a stable-oxide-forming additive element if it forms a stable oxide in a titanium-base composition, where the titanium-base composition either has substantially no oxygen in solid solution or where the titanium-base composition has a small amount of oxygen in solid solution. As much as about 0.5 weight percent oxygen in solid solution may be required for the stable-oxide-forming additive element to function as an effective stable-oxide former. Thus, preferably, the titanium-base composition has from zero to about 0.5 weight percent oxygen in solid solution. Larger amounts of oxygen may be present, but such larger amounts may have an adverse effect on ductility. In general, oxygen may be present in a material either in solid solution or as a discrete oxide phase such as the oxides formed by the stable-oxide-forming additive elements when they react with oxygen.

[0037] Titanium has a strong affinity for and is highly reactive with oxygen, so that it dissolves many oxides, including its own. The stable-oxide-forming additive elements within the scope of the present approach form a stable oxide that is not dissolved by the titanium metallic composition matrix during typical thermal conditions associated with reduction, consolidation, heat treat, and exposure. Examples of stable-oxide-forming additive elements are strong oxide-formers such as magnesium, calcium, scandium, and yttrium, and rare earths such as lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium, and mixtures thereof.

[0038] The presence and the nature of the distribution of the oxide particles 26 has several additional important consequences. The dispersion of oxide particles 26 serve to strengthen the matrix 22 by the dispersion-

strengthening effect and also to improve the elevated-temperature creep strength of the matrix 22. The dispersion of oxide particles 26 may also pin the grain boundaries 32 of the matrix 22 to inhibit coarsening of the grains 30 during processing and/or elevated temperature exposure. Additionally, in some circumstances the oxide particles 26 have a higher specific volume than the stable oxide-forming additive elements from which they are produced. This higher specific volume creates a compressive force in the matrix 22 near its surface. The compressive force inhibits crack formation and growth when the article is loaded in tension or torsion during service, a highly beneficial result.

[0039] One important utilization of the present approach is that the consolidated article may form an insert in relation to a mass of different material. In the embodiment of Figures 3-4, an insert 40 of the microscale composite 21 as discussed above is placed into the non-composite metallic alloy material that forms the balance of an airfoil 42 of a gas turbine blade 44. The insert increases the strength and modulus of the airfoil 42, without being exposed to the environmental gases and without altering the shape of the airfoil 42. Inserts may be incorporated by any operable approach, such as by making the non-boride portion by casting in place, casting and working, or a nonmelting approach.

[0040] Other examples of articles that may be made by the present approach include components of gas turbine engines include vanes, disks, blisks, blings, shafts, cases, engine mounts, seals, and housings. Other articles include, for example, airframe components, automotive parts, and biomedical articles. The use of the present invention is not limited to these particular articles, however.

[0041] Figure 5 depicts a preferred method for producing a metallic article made of constituent elements in constituent-element proportions. At least one nonmetallic precursor compound is furnished, step 50. All of the nonmetallic precursor compounds collectively contain the constituent elements in their respective constituent-element proportions. The metallic elements may be supplied by the precursor compounds in any operable way. In the preferred approach, there is exactly one non-oxide precursor compound for each metallic alloying element, and that one precursor compound provides all of the material for that respective metallic constituent in the metallic composition. For example, for a four-element metallic material that is the final result of the process, a first precursor compound supplies all of the first element, a second precursor compound supplies all of the second element, a third precursor compound supplies all of the third element, and a fourth precursor compound supplies all of the fourth element. Alternatives are within the scope of the approach, however. For example, several of the precursor compounds may together supply all of one particular metallic element. In another alternative, one precursor compound may supply all or part of two or more of the metallic elements. The latter approaches are less

preferred, because they make more difficult the precise determination of the elemental proportions in the final metallic material. The final metallic material is typically not a stoichiometric compound having relative amounts of the metallic constituents that may be expressed as small integers.

[0042] The precursor compounds are nonmetallic and are selected to be operable in the reduction process in which they are reduced to metallic form. In one reduction process of interest, vapor-phase reduction, the precursor compounds are preferably metal halides. In another reduction process of interest, solid-phase reduction, the precursor compounds are preferably metal oxides. Mixtures of different types of precursor compounds may be used.

[0043] Some constituents, termed "other additive constituents", may be difficult to introduce into the metallic composition. Whatever the reduction technique used in step 52 and however the other additive constituent is introduced, the result is a mixture that comprises the metallic composition. Methods for introducing other additive constituents may be performed on precursors prior to the reduction of the base-metal constituent, or on already-reduced material. For example, boron may be added using borane gas, or yttrium may be added as yttrium chloride.

[0044] The chemical composition of the initial metallic composition is determined by the types and amounts of the metals in the mixture of nonmetallic precursor compounds furnished in step 50 or that are introduced in the processing. The relative proportions of the metallic elements are determined by their respective ratios in the mixture of step 50 (not by the respective ratios of the compounds, but the respective ratios of the metallic elements). The initial metallic composition has more titanium than any other metallic element in the precursor compounds, producing a titanium-base initial metallic composition.

[0045] Optionally, the nonmetallic precursor compounds may be pre-consolidated, step 51, prior to chemical reduction by techniques such as solid-phase reduction. The pre-consolidation leads to the production of a sponge in the subsequent processing, rather than particles. The pre-consolidation step 51, when used, is performed by any operable approach, such as pressing the nonmetallic precursor compounds into a pre-consolidated mass.

[0046] The single nonmetallic precursor compound or the mixture of nonmetallic precursor compounds is chemically reduced to produce metallic particles or sponge, without melting the precursor compounds or the metal, step 52. As used herein, "without melting", "no melting", and related concepts mean that the material is not macroscopically or grossly melted for an extended period of time, so that it liquefies and loses its shape. There may be, for example, some minor amount of localized melting as low-melting-point elements melt and are diffusively alloyed with the higher-melting-point elements that do

not melt, or very brief melting for less than 10 seconds. Even in such cases, the gross shape of the material remains unchanged.

[0047] In one preferred reduction approach, termed vapor-phase reduction because the nonmetallic precursor compounds are furnished as vapors or gaseous phases, the chemical reduction may be performed by reducing mixtures of halides of the base metal and the metallic alloying elements using a liquid alkali metal or a liquid alkaline earth metal. For example, titanium tetrachloride, borane trichloride, and the halides of the metallic alloying elements are provided as gases. A mixture of these gases in appropriate amounts is contacted to molten sodium, so that the metallic halides are reduced to the metallic form. The metallic composition is separated from the sodium. This reduction is performed at temperatures below the melting point of the metallic composition. The approach, but without the present invention, is described more fully in US Patents 5,779,761 and 5,958,106, and US Patent Publication 2004/0123700. Other gas-phase techniques are described in US Publications 2004/0050208 and 2004/0261573.

[0048] Reduction at lower temperatures rather than higher temperatures is preferred. Desirably, the reduction is performed at temperatures of 600°C or lower, and preferably 500°C or lower. By comparison, prior approaches for preparing titanium- and other metallic compositions often reach temperatures of 900°C or greater. The lower-temperature reduction is more controllable, and also is less subject to the introduction of contamination into the metallic composition, which contamination in turn may lead to chemical irregularities. Additionally, the lower temperatures reduce the incidence of sintering together of the particles during the reduction step and limits the potential coarsening of the stable boride and optional oxide dispersions.

[0049] In another reduction approach, termed solid-phase reduction because the nonmetallic precursor compounds are furnished as solids, the chemical reduction may be performed by fused salt electrolysis. Fused salt electrolysis is a known technique that is described, for example, in published patent application WO 99/64638. Briefly, in this variation of in fused salt electrolysis the mixture of nonmetallic precursor compounds, furnished in a finely divided solid form, is immersed in an electrolysis cell in a fused salt electrolyte such as a chloride salt at a temperature below the melting temperature of the metallic composition that forms from the nonmetallic precursor compounds. The mixture of nonmetallic precursor compounds is made the cathode of the electrolysis cell, with an inert anode. The elements combined with the metals in the nonmetallic precursor compounds, such as oxygen in the preferred case of oxide nonmetallic precursor compounds, are partially or completely removed from the mixture by chemical reduction (i.e., the reverse of chemical oxidation). The reaction is performed at an elevated temperature to accelerate the diffusion of the oxygen or other gas away from the cathode. The cathodic

potential is controlled to ensure that the reduction of the nonmetallic precursor compounds will occur, rather than other possible chemical reactions such as the decomposition of the molten salt. The electrolyte is a salt, preferably a salt that is more stable than the equivalent salt of the metals being refined and ideally very stable to remove the oxygen or other gas to a desired low level. The chlorides and mixtures of chlorides of barium, calcium, cesium, lithium, strontium, and yttrium are preferred. The chemical reduction is preferably, but not necessarily, carried to completion, so that the nonmetallic precursor compounds are completely reduced. Not carrying the process to completion is a method to control the oxygen content of the metal produced and to allow subsequent formation of the oxide dispersion. If the pre-consolidation step 51 is performed, the result of this step 52 may be a metallic sponge.

[0050] In another reduction approach, termed "rapid plasma quench" reduction, the precursor compound such as titanium chloride is dissociated in a plasma arc at a temperature of over 4500°C. The precursor compound is rapidly heated, dissociated, and quenched in hydrogen gas. The result is fine metallic-hydride particles. Any melting of the metallic particles is very brief, on the order of 10 seconds or less, and is within the scope of "without melting" and the like as used herein. The hydrogen is subsequently removed from the metallic-hydride particles by a vacuum heat treatment. Oxygen may also be added to react with the stable-oxide-forming additive elements to form the stable oxide dispersion. Boron is added to react with titanium to produce a titanium boride.

[0051] Whatever the reduction technique used in step 52, the result is a material of a metallic titanium-base composition, titanium boride, and optionally stable oxide particles. The material may be free-flowing particles in some circumstances, or have a sponge-like structure in other cases. The sponge-like structure is produced in the solid-phase reduction approach if the precursor compounds have first been pre-compacted together (i.e., optional step 51) prior to the commencement of the actual chemical reduction. The precursor compounds may be compressed to form a compressed mass that is larger in dimensions than a desired final metallic article.

[0052] Optionally but preferably, the material is consolidated to produce a consolidated metallic article, step 54, without melting the titanium-base composition and without melting the consolidated titanium-base composition. The consolidation step 54 may be performed by any operable technique, with examples being hot isostatic pressing, forging, extrusion, pressing and sintering, and direct powder consolidation extrusion or rolling, or a combination of these methods.

[0053] Optionally but preferably, there is further processing, step 56, of the consolidated metallic article. In this processing, the article is not melted. Such further processing may include, for example, mechanically forming the consolidated metallic article, step 58, by any op-

erable approach, and/or heat treating the consolidated metallic article, step 60, by any operable approach, and/or oxidizing the consolidated metallic article, step 62, by any operable approach (where there are stable oxide-forming elements present that need to be reacted to form the oxide particles 26). These steps 58, 60, and/or 62, where used, are selected according to the nature of the titanium-base composition. However, these steps 58, 60, 62 are preferably performed at as low a temperature as possible to avoid excessive coarsening of the titanium boride particles 24 and 25.

[0054] The present approach has been practiced by preparing powders having compositions of titanium-about 0.8 weight percent boron-about 0.5 weight percent oxygen and titanium-about 2 weight percent boron-about 1 weight percent oxygen, using the preferred approach described above. Some powders were consolidated by hot isostatically pressing (HIP). Other powders were consolidated by HIP followed by extruding with an extrusion ratio of about 10:1. Some samples were stress relieved following consolidation.

[0055] Specimens were examined by X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. The X-ray diffraction identified the presence of alpha titanium and TiB. The scanning electron microscopy and transmission electron microscopy indicated the presence of a uniform fine distribution of sub-micron titanium boride particles, ranging in maximum dimension from less than 100 nanometers to several hundred nanometers. The intragranular titanium boride particles exhibited interfaces that were faceted with the adjacent matrix of alpha-phase titanium. The major zone axes of the TiB particles were aligned with the major zone axes of the adjacent alpha ( $\alpha$ )-phase titanium matrix. In this material, [11-20] $\alpha$  was parallel to [010] intragranular TiB, (0001) $\alpha$  was parallel to (001) intragranular TiB, and (-1100) $\alpha$  was parallel to (001) intragranular TiB. However, different relations may be found in other compositions.

[0056] The particles were plate-shaped and of similar shape, size, and orientation in both the as-HIP and HIP+extrude materials. Macrohardness measurements were conducted on both as-HIP and HIP+extruded materials. The materials were largely isotropic in both states, indicating that the extrusion did not produce a significant anisotropy in the hardness mechanical property.

[0057] Specimens were also prepared with titanium boride particles dispersed in a nominal Ti-6Al-4V matrix.

## 50 Claims

1. An article (20) comprising a microscale composite material (21) having a matrix (22) comprising more titanium by weight than any other element; and a dispersion of titanium boride particles (24, 25) in the matrix (22), wherein at least about 50 volume percent of the titanium boride particles (24, 25) have

a maximum dimension of less than about 2 micrometers.

2. The article (20) of claim 1, wherein the microscale composite material (21) has less than about 1.5 percent by weight boron. 5
3. The article (20) of claim 1, wherein the microscale composite material (21) has from about 1.5 percent by weight boron to about 17 weight percent boron. 10
4. The article (20) of claim 1, wherein the matrix (22) is polycrystalline with a grain size of less than about 10 micrometers. 15
5. The article (20) of claim 1, wherein the matrix (22) is polycrystalline, and wherein the titanium boride particles (24, 25) include intragranular titanium boride particles (24), and wherein the intragranular titanium boride particles (24) are crystallographically preferentially oriented relative to the matrix (22) within each grain (30). 20
6. The article (20) of claim 1, wherein the matrix (22) is polycrystalline, wherein the titanium boride particles (24, 25) include intragranular titanium boride particles (24), and wherein the intragranular titanium boride particles (24) within each grain (30) are coherent or partially coherent with the matrix (22) of said grain (30). 25 30
7. The article (20) of claim 1, wherein the microscale composite material (21) is mechanically within 20 percent of isotropic. 35
8. The article (20) of claim 1, wherein the titanium boride particles (24, 25) are plate-shaped.
9. The article (20) of claim 1, wherein the article (20) includes the microscale composite material (21) as an insert (40) in another material (44). 40
10. The article (20) of claim 1, wherein the microscale composite material (21) further includes a dispersion of oxide particles (26). 45

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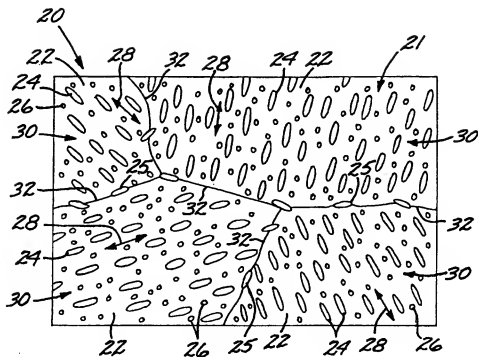


FIG. 1

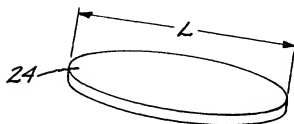


FIG. 2

FIG. 3

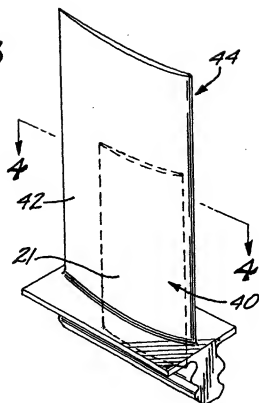
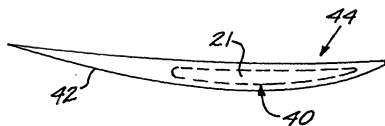


FIG. 4





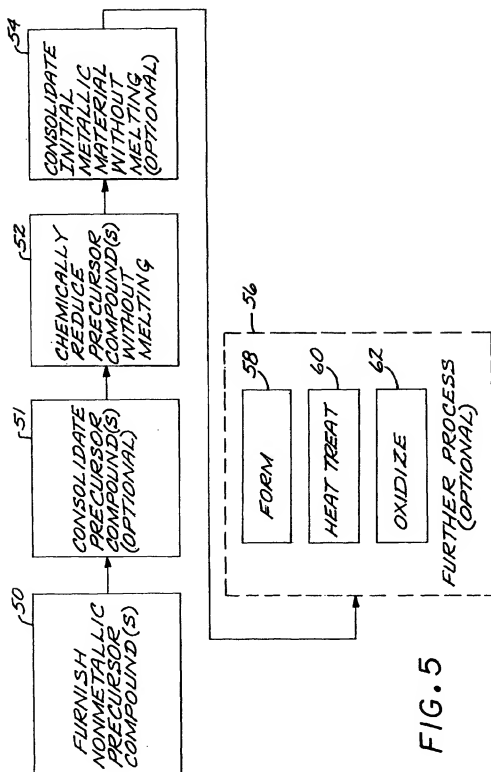


FIG. 5

FIG. 6

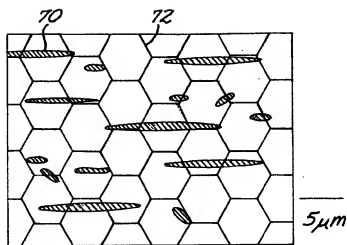


FIG. 7

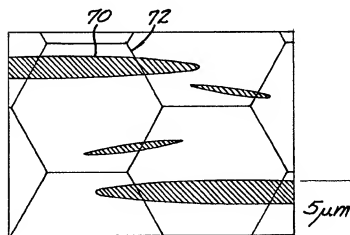
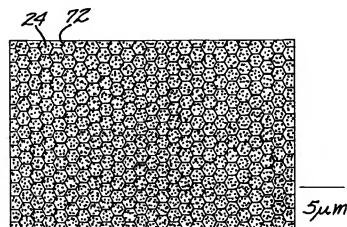


FIG. 8



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Application Number  
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EPC FORM 1501 (3-IP-04/01)

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3	Place of search Munich	Date of completion of the search 12 January 2006	Examiner Brown, A
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X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document			

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		& : member of the same patent family, corresponding document	

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 (51) Int. Cl. 7: B22D 1/00 (2006.01)

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/02



# PATENT SPECIFICATION

722,184

Date of filing Complete Specification Dec. 4, 1952.

Application Date Sept. 4, 1951.

No. 20894/51.

Complete Specification Published Jan. 19, 1955.

Index at acceptance:—Class 82(1), 14A2, 14A3(B: C), 14A4C, P3.

## COMPLETE SPECIFICATION

### Improvements in or relating to the production of Pure Titanium and Zirconium

We, JOSEPH PEFFO LEVY, a Turkish Citizen, of 1, Kathleen Avenue, Acton, London, W.3, DAVID HARRY PICKARD and LIONEL PICKARD, both British Subjects, and both of 223, St. John Street, London, E.C.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of titanium or zirconium metal in a high state of purity.

Titanium and zirconium are readily produced in the form of volatilizable chlorides by direct reduction of their ores with carbon in the presence of chlorine, but the production of the pure metal from the tetrachlorides is a matter of considerable difficulty owing to the great affinity of these metals for other substances, more particularly to their affinity for both the oxygen and nitrogen of the atmosphere, and for carbon and hydrogen. Even traces of impurities, particularly oxygen and nitrogen, may render the metal brittle and unworkable and of much less commercial value, although the metal is of great utility when in the pure condition.

Many processes have previously been suggested for obtaining pure titanium from the tetrachloride. Thus, it has been previously suggested to obtain titanium by reacting magnesium with titanium tetrachloride in accordance with the formula  $2\text{Mg} + \text{TiCl}_4 = 2\text{MgCl}_2 + \text{Ti}$  by introducing the titanium chloride vapour into molten magnesium, titanium being retained in a matrix of unreacted magnesium and magnesium chloride. It is extremely difficult, however, if not impossible, to remove all occluded titanium tetrachloride vapour, and in the subsequent leaching of the mass with water to remove magnesium chloride, this residual tetrachloride vapour is hydrolysed, giving insoluble oxides and oxychlorides which cannot be subsequently removed without attacking the titanium itself. Moreover, the leaching itself is a difficult operation to carry to completion and the titanium obtained by this process usually con-

tains at least 1% of impurities, mainly 60 because of the difficulty of leaching the solid matrix. The use of hydrochloric acid to remove unreacted magnesium may also introduce fresh impurities, since the hydrogen liberated may also act on very finely-divided titanium to form titanium hydride and impurities in the material normally used for lining the chamber may introduce further impurities which contaminate the titanium.

It has now been found that titanium and zirconium can be produced in a high state of purity without encountering the difficulties above referred to if the reduction reaction is carried out in the vapour phase in the presence of an inert gas (viz. one of the noble gases, in particular argon, helium or neon, on account of their availability) to act as an entrainment and effect the rapid removal and separation of the products of reaction.

It is also desirable, in order to avoid contamination by the walls of the reaction vessel of the titanium or zirconium metal when formed, to arrange for the reaction to take place in a reaction zone surrounded by moving inert gas and to carry away rapidly the reaction products as soon as formed to a cool zone without contact while hot with the walls of the vessel, and also to prevent mist particles of alkaline earth chloride from coalescing.

It will be shown hereinafter that the employment of a vapour phase reaction in conjunction with a moving inert gas entrainment not only avoids the difficulties hitherto encountered in obtaining pure metal, but also carries with it many advantages which could not have been foreseen.

Accordingly, in its broadest aspect, the present invention includes the process for the production of pure titanium or zirconium which comprises reacting the tetrachloride of the required metal in the vapour phase and in the presence of a moving inert gas with magnesium vapour, and passing the reaction products while entrained in the inert gas, through a zone sufficiently cool to solidify the magnesium chloride before the particles are allowed to settle.

The inert gas which may conveniently be

- argon on account of its availability is preferably employed as a vehicle to carry one or both of the reaction ingredients into the reaction zone as well as to carry the reaction products rapidly away from the reaction zone. The products of reaction are thus maintained in a finely-divided state in suspension until cool enough to be collected as a fine powder, and it is this feature of the invention which enables the titanium or zirconium metal to be separated from the magnesium chloride without the difficulties referred to above. Moreover, the inert gas acts to dilute the reaction ingredients and thereby enables the strongly exothermic reaction to be better controlled. It also sweeps away excess tetrachloride vapour and this is one of the many advantages of the use of a vapour phase reaction in conjunction with the employment of a moving inert gas. The higher temperature of the reaction provides a condition of greatly increased chemical activity. Furthermore, by reducing the tetrachloride with magnesium vapour, the reaction becomes practically quantitative, because at that temperature the products of reaction Ti or Zr+MgCl<sub>2</sub> are in the solid and liquid phases respectively and can thus be easily carried away by the entraining inert gas. This removal of the reaction products as rapidly as they are formed ensures that the reaction proceeds to completion and all the metal vapour is consumed leaving no residual matrix to be dissolved out as when conducting the reduction in the liquid phase. Furthermore, as will be shown hereinafter, the vapour phase reaction using an entraining gas enables a continuous process in a closed cycle to be carried out.
- In carrying out the invention, using the inert gas as a vehicle to carry the magnesium vapour forward, it may be caused to draw the vapour from a pool of boiling metal in a vessel surrounding the reaction vessel by passing it through a venturi and into the reaction vessel to meet a current of titanium or zirconium tetrachloride vapour. Ideal conditions obtain when the magnesium and the tetrachloride are in stoichiometric proportions, but a small excess of either reactant can be tolerated, and a slight excess of tetrachloride vapour over that required to maintain molar proportions prevents the tetrachloride vapour from striking back and acting on the surface of the pool of boiling magnesium. Any reaction of the surface of the molten magnesium makes it necessary to separate and recover the products of such reaction, with all the disadvantages hereinbefore mentioned. The inert gas passing through the venturi exerts a pumping action which carries the magnesium vapour into the reaction vessel very effectively.
- The reaction is strongly exothermic and the radiated heat may be utilised in maintaining the magnesium in a state of ebullition.
- The products of the reaction are obtained

in this way in the form of a finely-divided powder consisting of magnesium chloride and titanium or zirconium metal.

The deposition of both products of reaction in the form of a powder enables the metal to be extracted without difficulty. The reaction products do not come into contact with any wall surface until they are cool enough to remain uncontaminated.

Although argon is a comparatively expensive gas, very little is lost in the process, as the argon upon performing its function may be re-circulated after passing through condensers and heat exchangers which cool the gas and remove from it any excess tetrachloride. Thus, only small proportions of gas require to be introduced into the circuit from time to time to make good small losses which may occur.

In view of the necessity for keeping the molten magnesium out of contact with either oxygen or nitrogen of the atmosphere, the magnesium boiler may be fed with molten magnesium from a second heated vessel which is replenished by billets of solid metal. The tetrachloride is pressure-fed from a series of replenished storage tanks and the products of reaction are removed through an argon lock at convenient intervals without stopping the reaction.

The magnesium chloride can be easily removed and recovered from the titanium or zirconium metal in a condition which enables it to be economically returned to electrolytic cells for decomposition into metal and chlorine, both of which can be re-used in the process.

One specific method of carrying out the invention for the production of titanium in a continuous manner will now be described with reference to the accompanying drawing, which shows diagrammatically a form of reaction vessel with its accompanying melting vessel for supplying molten magnesium.

In the drawing the reaction vessel 10 is in the form of a cylinder, the sides of which at the top converge into the venturi throat 11, the upper part of the reaction vessel 10 being surrounded by concentric vessel 12 provided with a cover 13 which may be secured to the flange 14 by bolts (not shown) or otherwise. The reaction vessel is provided with a side inlet 15 passing through the outer vessel 12. Above the outer vessel 12 is a small box 16, provided with an inlet 17 and cover 19, through the bottom of which passes a tube 20 extending upwardly nearly to the top of the box 16 and downwardly through an aperture in the lid 13 terminating in a nozzle 21 situated centrally above the venturi throat 11. The outer vessel 12 communicates through the tube 22 near the bottom thereof with the bottom part of a melting vessel 23 closed with cover 24 in which is provided an inlet 25 of sufficient width to take billets of magnesium. The inlet 25 is closed with a cover 26. The



reaction vessel 10 is flanged at the bottom and attached to the wide cooling vessel 27 which is flanged top and bottom and the bottom flanged at 29 is bolted to the flanged inlet conduit 28 of the receiver 30 which has a narrower flanged outlet 31 bolted at 32 to the conduit 33 leading to an outlet 34 in the side of the cooling vessel 27. By means of the valves 35, 36, 37, 38 and 39, the receiver can be shut off from the rest of the apparatus for the purpose of uncoupling the receiver and changing it without opening it or the apparatus to communication with the outside atmosphere.

In operation the outer vessel 12 and the melting vessel 23 are enclosed in furnaces (not shown) which melt the magnesium metal introduced into the opening 26 and maintain the metal in 23 in a molten condition and that in the outer vessel 12 at the boiling point. The apparatus may be worked as a continuous process in which argon from a suitable storage is pumped into the box 16 at the inlet 17 and passes through a quantity of metallic calcium or other gettering material 18 and enters the outer vessel 12 through the delivery tube 20 and jet 21. The stream of argon emerging from the jet 21 and from thence into the venturi throat 11 sets up a pumping action which draws magnesium vapour from above the magnesium in the vessel 12 and carries it down the reaction vessel 10 where it meets a stream of titanium tetrachloride which enters through the inlet 15. An intense exothermic reaction is set up in the centre part of the reaction vessel 10 forming fine particles of titanium metal and a mist of magnesium chloride which is carried downwards and enters the cool zone 27 in the lower part of the apparatus where the magnesium chloride solidifies in powder form and the mixed powders are collected in the receiver 30. Argon containing excess tetrachloride passes out at 31 and enters a system of condensers for the removal of titanium tetrachloride which is passed to a suitable storage and the argon is re-circulated entering the apparatus again at 17. By closing the valves 35, 36, 37 and 38 and opening valve 39, the receiver may be changed periodically by undoing the attachments at 32 and 29, the argon circulation being uninterrupted through the short-circuiting valve 39.

The level of the molten magnesium in the outer vessel 12 is kept constant by addition of magnesium billets through the inlet 25 and the connection 22 enables molten magnesium to flow freely into the outer vessel 12 without air entering the apparatus.

The following is an example of an experimental batch carried out in an apparatus as above described:—

A gas-fired furnace was arranged to pre-melt billets of magnesium in the melting vessel 23 which could conveniently transfer

the molten metal at about 850° C. to the boiler 12 heated in a second similar furnace. 10 pounds of metal was contained in the magnesium boiler 12, the surface reaching to just below the venturi throat 11 which had a 70 diameter of  $\frac{1}{16}$ ". The nozzle 21 having a diameter of  $\frac{1}{16}$ " was situated above the venturi at a distance suitable for drawing into the reaction vessel magnesium vapour by the argon which is passed through it. The argon flow rate was  $\frac{3}{4}$  cubic feet per minute and the magnesium evaporation was 8 pounds per hour. The titanium tetrachloride corresponded to the molar proportion of 8 pounds per hour of magnesium. In this way the gas flow was maintained at the optimum value so that sufficient magnesium was drawn in to give practically complete reduction of the titanium tetrachloride during its passage through the reaction zone. Optimum conditions will obviously depend on maintaining the correct adjustment of nozzle diameter, venturi throat diameter, distance of the nozzle above the venturi and rate of argon flow and magnesium evaporation which require previous calculation and trial but it was found that with the apparatus used the evaporation of magnesium metal may vary between 6 and 18 pounds per hour and the molar proportion of titanium tetrachloride is introduced to correspond to the predetermined rate of magnesium evaporation. Under the conditions stated, the product is delivered as a fine discrete powder, the particle size of which was measured for one experiment and found to 100 vary between  $1/12,000$  of an inch and  $1/400$  of an inch.

It was also found that with the dimensions given above, anything under 2 cubic feet per minute of argon gave rise to a solid matrix, 105 and anything above 7 cubic feet per minute tends to give only partial reduction or scatters the product too rapidly in the apparatus to permit of easy cleansing of the argon.

It has been found that an electrostatic or 110 cyclone precipitator interposed in the argon circulating system is very effective in collecting the products of reaction and for the purpose of cleansing the argon from minute dust particles which it entrains. 115

What we claim is:—

1. A process for the production of pure titanium or zirconium which comprises reacting the tetrachloride of the required metal in the vapour phase and in the presence of a 120 moving inert gas with the vapour obtained by volatilizing magnesium, and passing the reaction products while entrained in the inert gas through a zone sufficiently cool to solidify the magnesium chloride before the particles 125 are allowed to settle.

2. A process as claimed in Claim 1, wherein the inert gas employed is argon.

3. A process as claimed in Claim 1 or Claim 2, wherein the inert gas is employed as a 130

vehicle to carry one or both of the reaction ingredients into the reaction zone and to carry the reaction products away therefrom.

4. A process as claimed in Claim 3, wherein the inert gas is employed as a vehicle to carry the magnesium vapour forward through a venturi and into a reaction vessel to meet a current of titanium or zirconium tetrachloride vapour.
- 10 5. A process as claimed in any one of the preceding claims, wherein the process is carried out in a closed cycle by passing the inert gas continuously through a jet above a venturi throat arranged in the top of the reaction vessel situated in an outer vessel containing the boiling magnesium and by passing the titanium or zirconium tetrachloride into the reaction vessel below the venturi, the reaction products being removed from time to time through an argon lock from a collecting vessel situated below the reaction vessel, and the inert gas being circulated through a condensing system to separate any titanium or zirconium tetrachloride and then re-cycled.
- 15 6. A process for the production of pure titanium or zirconium, substantially as described with reference to the accompanying drawing.

7. Pure titanium or zirconium whenever produced by the process as claimed in any one of the preceding claims.

8. Apparatus for carrying out the process

claimed in any one of Claims 1 to 6, comprising an upright reaction vessel of substantially greater height than width, the upper part of which is surrounded by a closed outer vessel for holding boiling magnesium, said reaction vessel converging at the top above the level of the molten magnesium in the outer vessel in a venturi throat and disposed centrally above the latter, an inlet pipe passing through the cover of the outer vessel and terminating in a nozzle, said inlet pipe being connected to a supply of argon, the said reaction vessel being also provided with an inlet for titanium or zirconium tetrachloride passing through the sides of the outer vessel and the reaction vessel and terminating within the latter at a point below, the venturi throat, the lower part of the reaction vessel opening into a cooling vessel and receiver, the said cooling vessel or the receiver being provided with an outlet for carrying away argon and excess titanium or zirconium tetrachloride.

9. Apparatus for carrying out the process claimed in any one of Claims 1 to 6, substantially as described with reference to the accompanying drawing.

For the Applicants:

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#### PROVISIONAL SPECIFICATION

#### Improvements in or relating to the production of Pure Titanium and Zirconium

- We, JOSEPH PEPPO LEVY, a Turkish Citizen, of 1, Kathleen Avenue, Acton, London, W.3, DAVID HARRY PICKARD and LIONEL PICKARD, both British Subjects, and both of 223, St. John Street, London, E.C.1, do hereby declare this invention to be described in the following statement:—

This invention relates to the production of titanium and zirconium metals in a high state of purity.

- Titanium and zirconium are readily produced in the form of volatilizable chlorides by direct reduction of their ores with carbon in the presence of chlorine, but the production of the pure metals from the chlorides is a matter of considerable difficulty owing to the great affinity of the metals for other substances, more particularly for their affinity for both the oxygen and nitrogen of the atmosphere and carbon and hydrogen as reducing agents. Even traces of impurities, particularly oxygen and nitrogen, may render the metals brittle and unworkable and of much less commercial value, although the metals are of great utility when in the pure condition.

- Many processes have previously been suggested for obtaining pure titanium from the

tetrachloride. Thus it has been previously suggested to obtain titanium by reacting magnesium with titanium chloride in accordance with the formula  $2\text{Mg} + \text{TiCl}_4 = 2\text{MgCl}_2 + \text{Ti}$  by introducing the titanium chloride vapour into molten magnesium, titanium being retained in a matrix of unreacted magnesium and magnesium chloride. It is extremely difficult, however, if not impossible, to remove all occluded titanium tetrachloride vapour, and in the subsequent leaching of the mass with hydrochloric acid to remove unreacted magnesium, this residual tetrachloride vapour is hydrolysed, giving titanous acid. Moreover the leaching itself is a difficult operation to carry to completion and the titanium obtained by this process usually contains at least 1% of impurities, mainly because of the difficulty of leaching the solid matrix. The use of hydrochloric acid may also introduce fresh impurities, since the hydrogen liberated may also form titanium hydride and impurities in the steel normally used for lining the chamber may introduce further impurities, especially carbon, which contaminate the titanium.

It has now been found that titanium and

zirconium can be produced in a high state of purity without encountering the difficulties above referred to if the reaction is carried out in the vapour phase in the presence of an inert gas (viz. one of the noble gases, in particular argon, helium or neon, on account of their availability) to act as an entrainment and effect the rapid removal and separation of the products of reaction.

10 It will be shown hereinafter that the employment of a vapour phase reaction in conjunction with an inert gas entrainment not only avoids the difficulties hitherto encountered in obtaining pure titanium or zirconium, but also carries with it many advantages which could not have been foreseen.

Accordingly, in its broadest aspect the present invention includes the process for the production of pure titanium or zirconium which comprises reacting the tetrachloride of the required metal entirely in the vapour phase and in the presence of an inert gas, with magnesium vapour and separating mechanically the titanium or zirconium metal particles formed from the magnesium chloride.

25 The inert gas serves as a vehicle to carry the vapours forward so that when the latter react there is no interruption to the forward movement. The importance of this will be seen when describing the invention specifically.

30 The inert gas employed may conveniently be argon on account of its availability.

The higher temperature of reaction provides a condition of greatly increased chemical activity. Moreover by reducing the tetrachloride with a metal vapour the reaction becomes practically quantitative because at that temperature the products of reaction  $Ti$  or  $Zr + MCl_2$  ( $M =$  reducing metal) are in the solid and liquid phases respectively and can thus be separated by physical means. This removal of the reaction products as rapidly as they are formed ensures that the reaction proceeds to completion and all the metal vapour

is consumed, leaving no residual matrix to be dissolved out as is the case when conducting the reduction in the liquid phase. Furthermore the vapour phase reaction using an entraining gas enables a continuous process in a closed cycle to be carried out.

The magnesium chloride may be submitted to electrolysis, being in the anhydrous condition, and the magnesium formed may be returned to the process and the chlorine used for preparing fresh tetrachloride.

60 It will be appreciated that in view of the affinity of all the metals concerned for both oxygen and nitrogen it is necessary to replace all air in the apparatus by the inert gas before commencing the operation.

The products obtained by the process of the invention are of exceptional purity, partly for the reasons already given, and partly because the employment of an inert gas maintains an inert atmosphere in the apparatus so that there is no detrimental action on the walls of the apparatus or on the products of reaction, as is the case in a liquid phase reaction. Moreover impurities which may be contained in the reducing metal employed, or which it may pick up from the containing vessel, will be left behind in the latter, and parts of the apparatus which would come in contact with hot tetrachloride vapour would be likely to suffer from corrosion, whereas by diluting this vapour with an inert gas this is avoided.

70 It is also a substantial advantage of the process of the invention that the magnesium chloride is obtained in a form in which it can be immediately recovered instead of in the form of a solution which may be too expensive to recover economically and yet be otherwise difficult to dispose of.

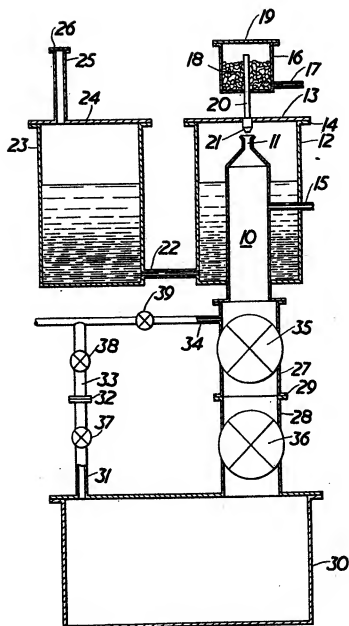
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# PATENT SPECIFICATION



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International Classification:—C22b, d.

## COMPLETE SPECIFICATION

### Process for the Production of Titanium

We, FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT, of Leverkusen-Bayerwerk, Germany, a Body Corporate organised under the Laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The present invention relates to a process for the production of titanium.

It is known that titanium halides can be reduced with alkali or alkaline-earth metals in order to obtain titanium. The reaction is 15 generally carried out by placing the alkali or alkaline-earth metal in a reaction vessel, heating to the reaction temperature of 700-900°C. and then introducing the titanium halide, using argon as a protective gas. The 20 titanium which is formed separates out in the form of a sponge. Moreover, during the reduction, there is also formed alkali metal halide or alkaline-earth metal halide which is present in the form of a melt at the reaction temperature and is run off through suitable devices after the reaction is completed. The halide which remains contained in the titanium sponge in addition to excess reduction metal is to a large extent distilled off 30 by heating the reaction vessel under vacuum. After this treatment, the titanium sponge is so firmly set in the reaction vessel that it has to be removed with the aid of mechanical devices such as milling devices or drills. 35 It has now been found that the reduction of titanium halide can be carried out technically in a substantially more simple manner if the reduction metal, i.e. alkali or alkaline-earth metal or metals, is used in the form of an alloy with zinc, cadmium or lead or a mixture of two or all of these metals, which alloy is liquid at the reaction temperature, and if the gaseous titanium halide is introduced into this liquid alloy. 45 The term alkaline-earth metal as used

[Price 3/6]

herein includes magnesium. The separated titanium is then suspended in the liquid alkali metal or alkaline-earth metal halide melt being simultaneously formed, settles satisfactorily in the said melt and can be 50 pumped off from the boundary layer between the liquid alloying metal and the alkali metal or alkaline-earth metal halide melt.

All titanium halides, but preferably 55 titanium chloride, can be used for the present process. The amount thereof which is added to the reduction metal is preferably such that the latter remains in excess in order to avoid reformation of titanium chloride in the alkali or alkaline-earth metal 60 chloride melt.

The process may be carried out, for example as follows:

The reduction metal, for example magnesium, is dissolved in liquid zinc, cadmium, lead or a mixture thereof and the gaseous titanium halide is thereafter introduced at the reaction temperature, which is in the region of 600°C. The introduction of the said 70 halide can be carried out with all technical devices known for such purposes. One preferred method consists in that the gaseous titanium chloride is forced into the metal melt through a bottom plate which is permeable to gas. 75

The separated titanium is suspended in the alkali or alkaline-earth metal chloride melt being simultaneously formed in the reaction, settles therein and may be pumped 80 off from the boundary layer between the alloying metal and the clarified alkali or alkaline-earth chloride melt. The alloy is advantageously covered from the outset with the corresponding chloride, for example calcium chloride. 85

The further working up process may consist in allowing the titanium-containing suspension which is pumped off to settle and then filtering off the titanium. The filter cake 90

containing titanium may be freed from the excess melt and the reduction and alloying metals, by heating the said cake, for example in a vacuum furnace heated by radiant heat.

5 The pure titanium sponge can be melted down in the usual manner.

One particular advantage of the process according to the invention consists in that the process may also be carried into effect 10 continuously. In this case, the alloy, consisting of the reduction metal and the alloying metal, is preferably prepared externally of the reaction vessel and the liquid alloy is caused to flow continuously through the 15 reaction chamber. The alloy, which issues from the reaction chamber and of which the content of reduction metal is to a large extent consumed, can be re-introduced into the cycle again after adding fresh reduction 20 metal.

The circulation of the alloy may either be effected with the aid of induction currents, which at the same time serve for heating purposes, or by mechanical means similar 25 to those known in connection with the circulation of metallic mercury in alkali metal chloride electrolysis cells. The liquid cathode metal in this case preferably runs over weirs, so that the electrolysis sludge is retained in 30 the cell, from which it may be extracted from time to time.

In one preferred form of the process according to the invention the reduction metal is produced in the required amount directly 35 within the alloy metal by fusion electrolysis, using the liquid alloy metal as cathode. The electrolyte used may consist of alkaline-earth or alkali metal chlorides or mixtures thereof or other fusion electrolytes, which can be 40 electrolysed to yield the alkaline-earth or alkali metal with which the titanium compounds are to be reduced.

The titanium suspension formed in the melt of the alkaline-earth or alkali metal 45 chlorides may also be pumped off continuously or intermittently, and can be worked up according to the process indicated above.

An additional advantage of the present process lies in the fact that the heat of reduction 50 liberated during the reduction may be dissipated by suitable cooling means either during circulation of the alloy or of the melt. By this means, it is possible to produce a high reaction velocity. At the same 55 time, it is also possible in a simple manner to control and regulate the maintenance of the required excess of reduction metal with respect to the titanium halides.

If necessary, the process can also be carried 60 into effect with exclusion of air or in an inert gas atmosphere.

#### EXAMPLE 1.

2000 gm. of cadmium are melted and 52 gm. of magnesium are added to this melt. 65 The metal melt is heated to 600°C. and

covered with a carnallite melt. Thereafter, titanium tetrachloride is introduced through the porous base of the vessel. During the reaction, there are formed 203 gm. of magnesium chloride and about 52 gm. of titanium metal in powder form, which settles in the carnallite melt and is removed as a suspension. The titanium suspension is filtered, the filter cake is liberated from excess melt and alloy metal in a vacuum furnace 75 which is provided with radiation heating and the titanium which is obtained is melted down in the usual manner in an arc furnace.

#### EXAMPLE 2.

A sodium chloride-calcium chloride melt 80 containing about 25% of NaCl and 75% of CaCl<sub>2</sub> is electrolysed in a suitable electrolysis cell resulting in the hourly production of 90-100 gm. of sodium and corresponding equivalent of calcium in the liquid 85 cathode which consists of cadmium metal. The cathode metal flows over weirs into a reaction vessel, in which the reduction metal is reacted with gaseous titanium tetrachloride, and then flows back into the cell. The 90 temperature in the electrolysis cell is 600-650°C. 190 gm. of gaseous titanium tetrachloride per hour are introduced into the reaction vessel through a gas permeable base plate. The amount of titanium tetrachloride 95 corresponds approximately to the amount of reduction metal which is hourly produced. When it enters the reaction vessel, the cathode metal contains about 5% of the reduction metal, and about 0.5 to 1%, thereof 100 on leaving the said vessel. In the reaction vessel, 48 gm. of titanium separate hourly as titanium powder and 240 gm. of common salt or corresponding calcium chloride equivalents are produced in the same period. The 105 current density in the electrolysis cell is 28,000-30,000 amp./m<sup>2</sup>, and the current efficiency 90-95%. The titanium suspension which separates in the reaction vessel in the alkaline-earth metal or alkali metal 110 chloride melt is extracted by vacuum from time to time from the reaction vessel, allowed to settle and filtered. The filter cake containing titanium is fed to a radiation furnace operated with vacuum. In this furnace, 115 the remaining melt and reduction metals are distilled off. The titanium which is obtained is thereafter melted down in an arc furnace in the usual manner. All operations are carried out with exclusion of air. 120

#### EXAMPLE 3.

The procedure followed in this example is in principle the same as that described in Example 2. Zinc is used instead of cadmium as the alloy metal and magnesium is electrolysed 125 into the zinc from a carnallite melt. 52 gm. of magnesium are separated out every hour and this is reacted in the reaction cell with the theoretical amount of titanium tetrachloride. 204 gm. of magnesium chloro-130

ride and 51 gm. of titanium metal are formed each hour. The temperature in the electrolysis cell is 700-750°C. As in Example 2, the operation is carried out with an excess of magnesium metal which remains in the cycle.

What we claim is:—

1. A process for the production of titanium from titanium halide by reduction with alkaline-earth or alkali metals, wherein at least one alkaline-earth or alkali metal is dissolved in zinc, cadmium or lead or a mixture of two or all of these metals to form a liquid alloy and the titanium halide is introduced into this liquid alloy.
2. A process as claimed in Claim 1, wherein the liquid alloy is covered with an alkaline-earth or alkali metal chloride melt, from which the titanium formed is pumped off.
3. A process as claimed in Claim 1 or 2, wherein the process is carried out continuously.

4. A process as claimed in any of Claims 1 to 3, wherein an excess of alkali or alkaline-earth metal is used in relation to the titanium halide.

5. A process as claimed in Claim 1, wherein the alkali or alkaline-earth metal is directly deposited in the alloying metal by fusion electrolysis.

6. A process for the production of titanium from titanium halide substantially as described with reference to any of the Examples.

7. Titanium whenever produced by the process claimed in any of the preceding claims.

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# EUROPEAN PATENT OFFICE

## Patent Abstracts of Japan

PUBLICATION NUMBER : 62065921  
PUBLICATION DATE : 25-03-87

APPLICATION DATE : 12-09-85  
APPLICATION NUMBER : 60200618

APPLICANT : TOHO TITANIUM CO LTD;

INVENTOR : ONO AKIO;

INT.CL. : C01B 31/30

TITLE : PRODUCTION OF TITANIUM CARBIDE

ABSTRACT : PURPOSE: To produce high-purity titanium carbide at a low cost by using high- purity titanium tetrachloride as a raw material and using magnesium as the reducing agent.

CONSTITUTION: Titanium tetrachloride, a carbon-contg. substance and magnesium are allowed to react with one another at 700~1,300°C in an inert atmosphere to form titanium carbide. Then magnesium and magnesium chloride are separated at 800~1,200°C by vacuum filtration. Then the titanium carbide is heated at 1,500~2,500°C.

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STN CA Caesar accession number : 1062

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DN - 107:179480

ED - Entered STN: 14 Nov 1987

TI - Manufacture of titanium carbide

IN - Murayama, Ryoji; Takemura, Seiichi; Sudo, Osamu; Takeda, Yutaka; Yamashita, Akishi; Okawa, Tsutomu; Ono, Akio

PA - Toho Titanium Co., Ltd., Japan

SO - Jpn. Kokai Tokkyo Koho, 5 pp.

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LA - Japanese

IC - ICM C01B031-30

CC - 49-5 (Industrial Inorganic Chemicals)

Section cross-reference(s): 57

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PN - JP62065921	A2	19870325	JP 1985-200618	19850912
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PRAI- JP 1985-200618	19850912
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CLASS

PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
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JP 62065921	ICM C01B031-30
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OS - CASREACT 107:179480

AB - TiCl<sub>4</sub> is treated with C-contg. compds. and Mg in inert gas at 700-1300.degree. to give Ti carbide; Mg and Mg chloride is vacuum-sepd. at 800-1200.degree.; and then the product is further heated at 1500-2500.degree. in inert gas or under reduced pressure. Ti carbide, useful as ceramic tools, cermets, raw materials for powder metallurgy, etc., is prepd. from byproduct from Ti manuf. Thus, TiCl<sub>4</sub> and CCl<sub>4</sub> were added dropwise, in 7 h, to a tube contg. Mg and Ar (heated to 800.degree.) and then cooled. Mg and Mg chloride were removed from the product by vacuum-sepn., the product was pulverized, molded, and heated 3 h at 1800.degree. in 10-2 Pa to give Ti carbide contg. free C 0.02, bonded C 19.00, O 0.02, and Mg 0.002%.

ST - titanium carbide ; magnesium reducing agent titanium chloride

IT - Carbon black, reactions

RL: RCT (Reactant) ; RACT (Reactant or reagent)  
(reaction of, with titanium chloride, for titanium carbide prepn., in presence of magnesium)

IT - 7439-95-4 , Magnesium, uses and miscellaneous

RL: USES (Uses)

(in titanium carbide prepn., from titanium chloride and carbon compd.)

IT - 12070-08-5P , Titanium carbide ( TiC )

RL: PREP (Preparation)

(prepn. of, from, titanium chloride and carbon compd., in the presence of magnesium)

IT - 7550-45-0, reactions

RL: RCT (Reactant) ; RACT (Reactant or reagent)

(reaction of, with carbon compds., in the presence of magnesium, for

# EUROPEAN PATENT CODE

## Patent Abstracts of Japan

PUBLICATION NUMBER : 05078762

PUBLICATION DATE : 30-03-93

APPLICATION DATE : 23-05-91

APPLICATION NUMBER : 03149816

APPLICANT : SUMITOMO LIGHT METAL IND LTD;

INVENTOR : SHIBUE KAZUHISA;

INT.CL. : C22C 1/05 C22C 14/00 C22C 32/00

TITLE : TIAL-BASED COMPOSITE MATERIAL HAVING EXCELLENT STRENGTH AND ITS PRODUCTION

ABSTRACT : PURPOSE: To provide a composite material based on a TiAl intermetallic compd. and having fine grains, no internal defect and excellent strength by a reactive sintering method.

CONSTITUTION: A powdery Ti-Al mixture having a compsn. consisting of 35-50 atomic % Al and the balance Ti is prep'd. and particles of one or more among  $TiB_2$ ,  $Al_2O_3$  and SiC having 0.05-20 $\mu$ m average particle diameter are added to the mixture by  $\leq 20$ vol.%. They are mixed and sintered by a reactive sintering method to obtain the objective TiAl-based composite material.

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## Method of making metals and other elements

### Bibliographic data

### Description

## Claims

INPADOC legal status

**Publication number:** JP10502418 (T)

**Publication date:** 1998-03-03

**Inventor(s):**

**Applicant(s):**

**Classification:**

- international:

C22B5/16; B22F9/28; C22B5/04; C22B34/00; C22B34/12;  
C22C1/00; **B22F9/16; C22B5/00; C22B34/00; C22C1/00;**  
(IPC1-7): C22B34/12; B22F9/28; C22B5/16; C22C1/00

- **European:**

B22F9/28; C22B5/04; C22B34/00; C22B34/12D2; C22B34/12H2B

**Application number:** JP19950506817T-19950725

**Priority number(s):** WO1995US10159 19950725; US19940283358 19940801

**Also published as:**

US5779761 (A)

WO9604407 (A1)

US2008199348 (A1)

RU2152449 (C1)

NO970444 (A)

[more >>](#)

**View INPADOC patent family**

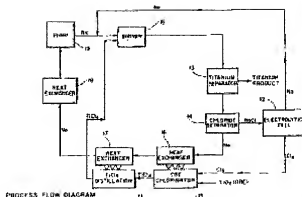
[View list of citing documents](#)

Abstract not available for JP 10502418 (T)

Abstract of corresponding document: **US 5779761 (A)**

A method of producing a non-metal element or a metal or an alloy thereof from a halide or mixtures thereof. The halide or mixtures thereof are contacted with a stream of liquid alkali metal or alkaline earth metal or mixtures thereof in sufficient quantity to convert the halide to the non-metal or the metal or alloy and to maintain the temperature of the reactants at a temperature lower than the lesser of the boiling point of the alkali or alkaline earth metal at atmospheric pressure or the sintering temperature of the produced non-metal or metal or alloy. A continuous method is disclosed, particularly applicable to titanium.

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## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-090692

(43)Date of publication of application : 06.04.1999

(51)Int.Cl.

B30B 9/14  
B01D 29/25  
B09B 3/00  
B30B 9/18

(21)Application number : 10-193768

(71)Applicant : CHIYODA CORP  
ISHIGAKI:KK

(22)Date of filing : 24.06.1998

(72)Inventor : KIMURA TAKASHI  
TOYAMA TATSUYA  
NOMI KENJI  
HASHIMOTO HIDEO  
MITANI YUKITOSHI

(30)Priority

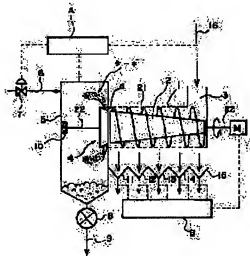
Priority number : 09183064 Priority date : 24.06.1997 Priority country : JP

## (54) SCREW PRESS

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a screw press which may be operated under an increased supply pressure on the raw material to be treated.

SOLUTION: This screw press has a filter cylinder 1 and a screw 2 inserted and disposed therein and has the functions to discharge the separated liquid outside through the peripheral wall of the filter cylinder by compressing the raw material to be treated supplied into the filter cylinder 1 by the screw 2 and to discharge filter cake outside from the spacing part 3 formed at the front end of the filter cylinder 1. The screw press has a pressurizing chamber 5 which encloses the spacing part



(a) formed at the front end of the filter cylinder 1. The pressurizing chamber 5 has a pressurized gas supply port and a filter cake discharge port.

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#### LEGAL STATUS

[Date of request for examination] 10.06.2002

[Date of sending the examiner's decision of rejection] 07.02.2006

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

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CLAIMS

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[Claim(s)]

[Claim 1] By having the screw by which insertion arrangement was carried out in a filtration cylinder and its interior, and squeezing with a screw the processed raw material supplied in the filtration cylinder in the screw press which has the function to make a supernatant liquid discharge to the exterior through the filtration cylinder circumference wall, and to make a filter cake discharge to the exterior from the gap section formed at the tip of a filtration cylinder (i) It is the screw press characterized by to have the pressurized room which surrounds the gap section formed at this tip of a filtration cylinder, and (ii) this pressurized room having pressurization gas supply opening and a filter cake exhaust port.

[Claim 2] The screw press of claim 1 which has a differential pressure regulatory mechanism for adjusting the differential pressure of a processed feeding pressure and pressurized-room internal pressure.

[Claim 3] Claim 1 which has the amount distribution measurement device of filtrate in which the shaft orientations of a filtration cylinder were met, or 2 screw presses.

[Claim 4] The screw press of claim 3 constituted so that the rotational frequency of a screw might be controlled according to the amount distribution of filtrate in alignment with the shaft orientations of a filtration cylinder.

[Claim 5] One screw press of claims 1-4 whose screws are what does not have a screw wing in the point.

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[Translation done.]

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2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a screw press.

[0002]

[Description of the Prior Art] The screw press is known as a filter for filtering the mixture (slurry liquid) of a solid particulate and a liquid. When this screw press has the screw by which insertion arrangement was carried out in a filtration cylinder and its interior and a processed raw material is supplied to them from feeding opening of that filtration cylinder, that processed raw material That rotation screw squeezes, the supernatant liquid produced by this squeezing is discharged outside through the bore of a large number formed in that filtration barrel wall, and, on the other hand, the filter cake produced by that squeezing is extruded and discharged from the gap section for filter cake discharge formed at that tip of a filtration cylinder. By the way, although such a screw press is usually operated under ordinary pressure thru/or pressurization, the filtration velocity in this case improves, so that that processed raw material supply pressure becomes high. However, if the supply pressure became high too much, since a part of supernatant liquid would produce the so-called liquid omission phenomenon leaked with a filter cake from the tip gap section, even if the supply pressure was high, about [ 0.5kg/cm<sup>2</sup> ] G were a limit.

[0003]

[Problem(s) to be Solved by the Invention] This invention makes it the technical problem to offer the screw press which can be operated by the raised processed raw material supply pressure.

[0004]

[Means for Solving the Problem] this invention persons came to complete this invention, as a result of repeating research wholeheartedly that said technical problem should be solved. Namely, by according to this invention, having the screw by which insertion arrangement was carried out in a filtration cylinder and its interior, and squeezing with a screw the processed raw material supplied in the filtration cylinder In the screw press which has the function to make a supernatant liquid discharge to the exterior through the filtration cylinder circumference wall, and to make a filter cake discharge to the exterior from the gap section formed at the tip of a filtration cylinder (i) The screw press characterized by to have the pressurized room which surrounds the gap section formed at this tip of a filtration cylinder, and (ii) this pressurized room having pressurization gas supply opening and a filter cake exhaust port is offered.

[0005]

[Embodiment of the Invention] The screw press of this invention is explained in full detail with a drawing. Drawing 1 shows the explanation block diagram of the screw press of this invention. drawing 1 -- setting -- 1 -- a filtration cylinder and 2 -- a screw and 3 -- in processed feeding opening and 4, a filtrate uptake member and 21 show a screw wing, and, as for a presser and 5, a shows the gap section for filter cake discharge, as for a pressurized room, and 11-15. The filtration cylinder 1 usually becomes a peripheral wall from the metal barrel which has many bores. A screw 2 consists of \*\*\*\*\* which has the spiral screw wing 21. That shaft diameter becomes large towards that point, and, as for this screw 2,

is squeezed by such big pressure that a processed raw material goes to the point of a filtration cylinder. The screw shaft 22 is attached to a screw 2, the edge of the screw shaft of one of these is connected with Motor M, the screw shaft of the another side penetrates the core of a presser 4, and the edge is supported by bearing 10. A presser 4 is the board of a truncated-cone configuration, arrangement immobilization is carried out at tip opening of the filtration cylinder 1, and the annular space section a for filter cake extrusion discharge is formed between the periphery edge of the presser, and a filtration cylinder internal surface. By advancing a presser 4, the clearance between the gap sections a (path clearance) can be narrowed, and the clearance between the gap sections a can be \*\*\*\*(ed) by on the other hand reversing it. This thing is not illustrated, although the pressure regulatory mechanism of the common use which consists of cylinders operated with pneumatic pressure or oil pressure is attached to that presser 4 in order to make a presser 4 \*\* approximately. The screw press which consists of a presser 4 arranged by the above mentioned filtration cylinder 1, the screw 2 arranged in the interior, and tip opening of the filtration cylinder is conventionally well-known.

[0006] In such a screw press, if a processed raw material is supplied from the feed hopper 3, the processed raw material will be fed by rotation of the screw 2 by Motor M in the direction of a tip in the inside of a filtration cylinder. In this case, since it has expanded as the shaft diameter of a screw 2 goes in that direction of a tip, a processed raw material will be squeezed by the bigger pressure. The liquid in a processed raw material is separated by this squeezing, this sejunction water flows into the exterior as filtrate through the bore of a large number formed in the peripheral wall side in that filtration cylinder, it decreases toward the direction of a tip of a filtration cylinder, and from the filtration cylinder tip gap section a, a filter cake is extruded and the liquid content in a processed raw material is discharged. As it is the above, when carrying out the expression of the processed raw material and separating into filtrate and a solid-state, the solid-liquid-separation rate can be raised by raising the supply pressure of a processed raw material. However, if this supply pressure becomes high too much, the liquid omission phenomenon which a supernatant liquid leaks through the detailed opening in the filter cake which exists in the tip gap section of that filtration cylinder will come to arise. When such a liquid omission phenomenon comes to arise, it becomes impossible to already perform smooth solid liquid separation. Therefore, the conventional screw press is operated by the processed raw material supply pressure which does not produce the liquid omission phenomenon, usual, and the supply pressure 0.5kg/cm<sup>2</sup> or less.

[0007] Even if the screw press of this invention raises and operates a processed raw material supply pressure, as shown in drawing 1, it is characterized by having the pressurized room 5 which surrounds the tip gap section a of the filtration cylinder 1, so that said liquid omission phenomenon may not arise. This pressurized room consists of proof-pressure containers, and especially that configuration is not restrained. Pressure gas supply opening is formed in said pressurized room 5, and the pressure gas supply line 6 is connected with the feed hopper. Moreover, the filter cake exhaust port for discharging to outdoor the filter cake discharged from the gap section a is arranged in this pressurized room 5, and the filter cake exhaust pipe 9 is connected with this exhaust port through the filter cake discharge device 8. This discharge device 8 can consist of a closing motion bulb for making the filter cake in a pressurized room discharge to outdoor, and can make an indoor filter cake discharge to outdoor by that disconnection. The conventionally well-known solid matter discharge device in which it is used as such a cake discharge device in order to discharge the solid matter in a tank to the exterior is employable.

[0008] When carrying out filtration processing of the processed raw material using the screw press of this invention, pressure gas is supplied in a pressurized room 5 from the pressure gas supply line 6, the differential pressure between the internal pressure force and supply pressure of the processed raw material is held in the predetermined range, and generating of the liquid omission phenomenon through the filter cake which exists in the gap section a is made to control. As pressure gas in this case, various kinds of gas, such as nitrogen gas, air, and carbon dioxide gas, is used. The pressure in a pressurized room 5 is selected corresponding to a processed raw material supply pressure, and, generally the pressure of the range of a pressure [ low about 0.5kg/cm<sup>2</sup> ] high about 0.5kg/cm<sup>2</sup> and the range of a desirable pressure to a pressure [ lower about 0.3kg/cm<sup>2</sup> than the supply pressure ] high about 0.3kg/cm<sup>2</sup> is chosen from the supply pressure. Moreover, the supply pressure of a processed raw



material is usually more than 0.1kg/cm<sup>2</sup>G preferably more than 0.01kg/cm<sup>2</sup>G. Moreover, the upper limit of the supply pressure is below 3kg/cm<sup>2</sup>G preferably below 5kg/cm<sup>2</sup>G. In the case of the screw press of this invention, it is usually desirable to operate it by the supply pressure of 0.1-3kg/cm<sup>2</sup>G. [0009] In the screw press of this invention, in order to make the pressure in a pressurized room 5 correspond automatically to a processed raw material supply pressure, it is desirable to make the differential pressure regulatory mechanism A connect. The pressure adjustable valve 7 which attached the differential pressure regulatory mechanism A to the pressure gas supply line 6 in drawing 1 , While connecting with the pressure sensor attached to the pressurized room 5, and the pressure sensor attached to the processed feeding tubing 16 and detecting the processed raw material supply pressure and pressurized-room internal pressure Based on the detected pressure force, the pressure adjustable valve 7 attached to the pressure gas supply line 6 is operated, and the differential pressure between pressurized-room 5 internal pressure and a processed raw material supply pressure is automatically adjusted to predetermined within the limits. The thing of common use is used as a differential pressure regulatory mechanism A in this case, and a computer etc. can constitute.

[0010] In the screw press of this invention, the supernatant liquid produced by squeezing of a processed raw material flows out of the peripheral wall side of the filtration cylinder 1 into the exterior as filtrate. In this case, the solid-state concentration in a filtration cylinder is changed in accordance with the shaft orientations of that filtration cylinder, and it is distributed so that it may increase toward that direction of a tip. In order to carry out stable operation of the screw press, it is desirable to operate so that this solid-state concentration distribution may be kept constant. In order to hold said solid-state concentration distribution uniformly, it is effective to adjust the rotational frequency of a screw so that the flow rate distribution in alignment with the shaft orientations of the filtrate which flows out of the peripheral wall of a filtration cylinder may be measured and flow rate distribution of this filtrate may become fixed. In drawing 1 , 11, 12, 13, 14, and 15 are uptake members which carry out uptake of the filtrate which flows out along with the longitudinal direction of the filtration cylinder 1. The thing of arbitration is usable if it is the thing of the container configuration which can carry out uptake of the filtrate which flows out of a filtration cylinder as this uptake member. Although the filtrate by which uptake was carried out to each of these uptake members is further discharged and collected from that uptake member outside, in order that it may acquire the flow rate distribution over the shaft orientations of the filtration cylinder of filtrate in this case, the flow rates Y11, Y12, Y13, Y14, and Y15 per [ by which uptake was carried out to each uptake member ] unit time amount are measured, respectively. Measurement of this filtrate flow rate can be measured with the flowmeter connected to the filtrate exhaust pipe connected with each uptake member. The flow rate in this case may be any of capacity or weight. Those hydrometry values are sent to the filtrate flow rate distribution measurement device B as an electrical signal, and flow rate distribution is measured here. Moreover, this filtrate flow rate distribution device B has the function to adjust that flow rate distribution, and the rotational frequency of Motor M is adjusted so that the flow rate distribution which this measurement flow rate distribution was contrasted with the flow rate distribution defined beforehand, and was measured may be in agreement with that flow rate distribution defined beforehand. Although the number of installation of a filtrate uptake member is suitably defined according to the die length of the filtration cylinder 1, generally it is two or more pieces, and is three or more pieces preferably.

[0011] In the screw press of this invention, it is desirable to use the screw which does not have the screw wing 21 in the point of a screw. When using for the point of such a screw the screw which omitted arrangement of a screw wing, a non-wing band without a screw wing is formed in the point of a filtration cylinder. When this non-wing band acts as a consolidation band of a cake, gathers the rotational speed of a screw and filtration velocity is raised, since a filter cake is compressed into shaft orientations into this non-wing band and the shaft-orientations consistency of that cake rises, a liquid omission phenomenon is prevented effectively. Therefore, the raw material supply pressure raised more is employable. In this invention, it is the distance which met the medial axis of a screw towards the back end of a screw from the tip (tip of a filtration cylinder) of a screw, and it is good to consider as the non-wing band which does not have a screw wing preferably in the between to the location of the arbitration

within the limits of 5-30cm from the screw tip to the location of the arbitration within the limits of 5-50cm.

[0012] The screw press of this invention is applied as a filter (solid-liquid separator) of the various mixture containing a liquid and a solid-state. The mixture of a waste plastic particle and a hydrocarbon oil, the water slurry liquid containing a solid particulate, the aqueous slurry liquid of a seed that extracts and contains the mixture of \*\* and fats and oils, water sludge, and a calcium carbonate are included by such mixture. The screw press of this invention may be which format of a \*\* type and a horizontal type.

[0013]

[Example] Next, an example explains this invention to a detail further. In addition, % shown below is weight %.

[0014] It considered as the example 1 plastic-waste model, and the plastics mixture which consists of 1% of polyvinylidene chlorides, polyethylene terephthalate:5%, and ABS-plastics:4% was crushed polyethylene:35%, polypropylene:30%, polystyrene:20%, and polyvinyl chloride:5% in the shape of a particle (average dimension: about 20mm). Next, the mixture (mixed weight ratio =1/0.9/0.6) of polyethylene, polypropylene, and polystyrene was added at a rate of 20 weight sections to the pyrolysis light-oil 100 weight section pyrolyzed and obtained, and this debris was heated for 30 minutes at 130 degrees C under churning. By this actuation, it dissolves and a part of polyvinylidene chloride dissolves the polyethylene, polypropylene, and polystyrene in debris. On the other hand, a polyvinyl chloride, polyethylene terephthalate, and ABS plastics remained in the solution by the shape of a non-dissolved particle. Filtration processing was carried out using the screw press of the structure which showed this to drawing 1, using the solution containing this non-dissolved plastics particle as a processed raw material. In this case, that processed raw material supply pressure was set to 1kg/cm<sup>2</sup>G, and the pressure of a pressurized room was set to 1kg/cm<sup>2</sup>G. In said filtration processing, the filter cake of a plastics particle was smoothly discharged from the gap section a at the tip of a filtration cylinder, and the liquid omission phenomenon was not produced at all. Moreover, uptake of the solution containing the plastics as filtrate was carried out to the filtrate uptake members 11-15. The filtrate capacity by which uptake was carried out to each uptake member was measured, and the filtrate flow rate distribution map to the shaft orientations of a filtration cylinder was created. Flow rate distribution of filtrate performed filtration processing by said screw press by adjusting the rotational frequency of Motor M so that it might be in agreement with this flow rate distribution map.

[0015] In example 2 example 1, from the tip before 50mm experimented using the screw which does not have a screw wing, using the thing of 100mm of diameters of a screen as a screw of the screw press of this invention, using the solution containing a non-dissolved plastics particle as a processed raw material. Consequently, even when the rotational speed of a screw was doubled and filtration velocity was gathered to the screw which has a screw wing to a tip, as shown in the following table, it was not generated at all but the liquid omission phenomenon was able to perform efficient filtration actuation. This is based on the degree to which consolidation of the filter cake is carried out rather than the case of an example 1 by the point in a filtration cylinder increasing by removing the point of a screw.

[0016]

[Table 1]

ケース	スクリューの 先端部の羽根	スクリューの 回転数 [rpm]	プレッシャーの 圧力 [kg/cm <sup>2</sup> G]	供給圧力 [kg/cm <sup>2</sup> G]	濾過速度 [kg/hr]
実施例 1	あり	0.8	4.0	1.0	55
実施例 2	50 mm カット	1.0	4.0	1.0	120

[0017] Filtration processing was performed like the example 1 using the water slurry liquid which contains a calcium-carbonate particle (pitch diameter of 20 micrometers) 20% as an example 3 processed raw material. In this case, the processed raw material supply pressure was set to 3kg/cm<sup>2</sup>G, and pressurized-room internal pressure was set to 3kg/cm<sup>2</sup>G. Also in such conditions, filtration actuation was able to be performed smoothly, without producing a liquid omission phenomenon.

[0018]

[Effect of the Invention] according to the screw press of this invention -- the supply pressure of a

processed raw material -- liquid omission phenomenon student \*\*\*\* -- high filtration velocity can be obtained from the ability for it to hold highly without things and to be operated. Therefore, in this invention, though it is small, the screw press of high throughput can be obtained.

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[Translation done.]

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## METHOD FOR PRODUCING TITANIUM

## Bibliographic data

Mosaics

Original document

INPADOC legal status

Publication number: JP2001279345 (A)

Publication date: 2001-10-10

Inventor(s): NAKAHARA NAOFUMI; YAMAGUCHI MASANORI

Applicant(s): TOHO TITANIUM CO LTD

## Classification:

- International: C22B34/12; C22B9/04; C22B9/22; C22B34/00; C22B9/00;  
C22B9/16; (IPC1-7): C22B34/12; C22B9/04; C22B9/22

## - European:

Application number: JP20000093558 20000330

Priority number(s): JP20000093558 20000330

Also published as:

 JP3671133 (B2)

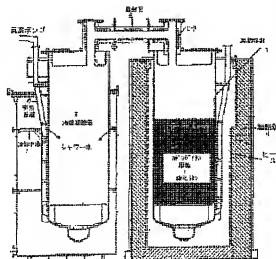
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## Abstract of JP 2001279345 (A)

**PROBLEM TO BE SOLVED:** To provide a method for producing titanium of high grade and stable quality extremely small in the content of impurities such as chlorine and magnesium by which the content of oxygen in titanium can stably be controlled, and additionally, impurities in sponge titanium can efficiently be separated.; **SOLUTION:** In this method for producing titanium, sponge titanium powder (preferably, sponge titanium powder for reseparation) with the average particle size of 1 to 50 mm and titanium oxide powder are mixed, and the powdery mixture is subjected to heating treatment under the reduced pressure in a heating vessel 1 to produce titanium oxide powder-sintered sponge titanium powder in which the titanium oxide powder particles are sintered around the sponge titanium powder particles, and, after that, the titanium oxide powder-sintered sponge titanium powder is dissolved to produce titanium in which the content of oxygen is controlled. In the case of sponge titanium powder for reseparation, impurities are efficiently separated and removed into a cooling condenser 2.



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(12) 公開特許公報 (A)

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(P2001-279345A)

(43) 公開日 平成13年10月10日(2001.10.10)

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C 22 B 34/12 9/04 9/22	1 0 3	C 22 B 34/12 9/04 9/22	1 0 3 4 K 0 0 1

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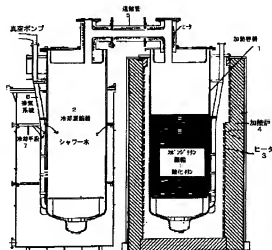
Fターム(参考) 4K001 A427 B423 D411 F413 J402

(54) 【発明の名称】 チタンの製造方法

(57) 【要約】

【課題】 チタン中の酸素含有量を安定して調整でき、  
加えてスポンジチタン中の不純物を効率よく分離でき、  
塩素やマグネシウム等の不純物が極めて少ない高品位で  
ありかつ品質の安定したチタン製造方法の提供。

【解決手段】 平均粒径1～50mmのスポンジチタン  
粉末(好ましくは再分離用スポンジチタン粉末)と酸化  
チタン粉末とを混合し、減圧下で加熱容器1において加  
熱処理して、酸化チタン粉末粒子がスポンジチタン粉末  
粒子周囲に焼結した、酸化チタン粉末焼結スポンジチ  
タン粉末を生成した後、該酸化チタン粉末焼結スポンジチ  
タン粉末を溶解して、酸素含有量を調整したチタンを製  
造することを特徴とするチタンの製造方法。再分離用ス  
ポンジチタン粉末の場合、不純物が冷却凝縮器2に効率  
よく分離・除去される。



## 【特許請求の範囲】

【請求項1】 平均粒径1〜50mmのスポンジチタン粉末と酸化チタン粉末とを混合し、減圧下で加熱処理して、酸化チタン粉末粒子がスポンジチタン粉末粒子周囲に焼結した、酸化チタン粉末焼結スポンジチタン粉末を生成した後、該酸化チタン粉末焼結スポンジチタン粉末を溶解して、酸素含有量を調整したチタンを製造することを特徴とするチタンの製造方法。

【請求項2】 前記スポンジチタン粉末が四塩化チタンを金属マグネシウムで還元して生成させた塊状スポンジチタンを平均粒径1〜50mmの顆粒に調整した再分離用スポンジチタン粉末であることを特徴とする請求項1に記載のチタンの製造方法。

【請求項3】 前記酸化チタン粉末に含まれるFe、Al、SiおよびNaが各々20ppm未満でありかつClが500ppm未満であることを特徴とする請求項1乃至2に記載のチタンの製造方法。

【請求項4】 前記酸化チタン粉末粒子がスポンジチタン粉末粒子周囲に焼結した酸化チタン粉末焼結スポンジチタン粉末を容器内に充填し、次いで容器内をアルゴンガスに置換した後、減圧雰囲気下で加熱処理することを特徴とする請求項1乃至2に記載のチタンの製造方法。

【請求項5】 前記加熱処理の温度が600〜1100℃にあることを特徴とする請求項1乃至2に記載のチタンの製造方法。

【請求項6】 前記溶解が電子ビーム溶解により実施されることを特徴とする請求項1乃至2に記載のチタンの製造方法。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、チタン中の酸素含有量を安定して調整することのできるチタンの製造方法に関するものであり、特に酸素含有量を安定して調整し、且つスポンジチタン中の不純物の分離を効率よく行い、塩素やマグネシウム等の不純物が極めて少ない高品位でありかつ品質の安定したチタンインゴットを得るためのチタンの製造方法に関する。

## 【0002】

【従来の技術】金属チタンは、耐食性などの優位性から幅広い用途の材料として用いられている。特に航空機用の材料に用いられる金属チタンは、安全性の面で高品質でかつ安定した品質が求められる。また、近年のVLSIに代表される半導体工業の急速な進歩のなかで、例えば、16〜64MビットDRAM等のSi MOS (Metal Oxide Semiconductor) メモリー等の半導体素子やバリヤ材などに用いられるスパッタリング用チタンターゲットには、特に極めて高い純度のものが要求される。

【0003】一般に金属チタンの品質を安定させるため、チタン中に含まれる酸素や鉄など成分を調整してい

る。例えば、強度アップを図って酸素含有量を高めることが行われている。酸素含有量については、スポンジチタンなどの顆粒状やチップ状の溶解原料を溶解して一旦ブリケットやロッドなどに成形する必要がある場合には、酸化チタンなどの含酸素原料を混合し溶解する。しかしながら、ブリケットやロッドなどの成形を必要としないハース溶解でインゴットを製造する場合に於ては、電子ビーム溶解方法では、スポンジチタンなどの顆粒状やチップ状の溶解チタン原料と酸化チタン粉末などを単に混合し溶解に供している。即ち、図3に示すように、上部に電子ビーム銃Gを装置しそして水冷銅モールドMを内部に納置した電子ビーム溶解炉Fにおいて、ホッパHから電子銃の下で且つモールドの上端近くまで伸延する水平コンベアCを通してスポンジチタンが供給され、スポンジチタンは先端から次々と電子ビームにより溶解されてモールド中に落下して上部部にチタンプールを形成しつつ冷却されてインゴットを形成する。その際、酸化チタンは、例えばホッパ内にスポンジチタンと一緒に供給される。丸印で拡大して示すように、スポンジチタン粒子は酸化チタン粉末によりまぶされたような状態でホッパ内に貯蔵され、水平コンベアにより搬送され、両者はコンベア先端部で電子ビームにより溶解される。しかしながら、この方法では、溶解中に酸化チタンなどの粉末状の含酸素原料が電子ビームの衝撃作用により炉内に上向き矢印で示すように飛散したり、スポンジチタンに含酸素原料が付着せずに分離してしまい、安定的に最終的なチタン中の酸素含有量を制御することは困難であった。チタンインゴット縦方向を通して酸素濃度分布の不均一が生じるなど不都合を生じた。

【0004】この問題を解決するために、例えば特開平1-156434号公報および特開平1-156435号公報では、電子ビーム溶解を行うに当たり、酸素あるいは鉄を含む溶液をチタン原料に浸漬法により予め付着させ、乾燥させて成分調整を行った後、溶解に供することによってチタンの成分調整を行うことが開示されている。上記方法では、チタン中の酸素や鉄含有量を上昇させることは可能であるが、酸素や鉄の溶液にチタンを浸漬させ表面に付着させるだけため、チタン中に含有させる酸素や鉄の量は任意に制御できず、結果として所望の成分含有量にすることは困難であった。

【0005】一方、クロール法によるスポンジチタンの製造工程は、四塩化チタンと金属マグネシウムを高温で反応させ、塊状スポンジチタンと塩化マグネシウムを生成させる還元工程と、さらに、塩化マグネシウムと未反応の金属マグネシウムを、減圧下で高温加熱することにより蒸発させ、塊状スポンジチタンから分離し除去する分離工程から成る。

【0006】塊状スポンジチタンから塩化マグネシウムと未反応の金属マグネシウム蒸気を分離除去する工程は、その分離がなかなか難しいため、工夫を要する。そ

の方法として、例えば特開昭57-185940号公報には、下部を電熱炉内に挿入して設置される縦型の円筒状レトリートにおいて、その下部にチタンなどの生成金属、副生塩化物及び未反応還元剤金属を保持する還元反応容器を収容しそしてその上部に排気手段と下部からの気化物を凝固するための冷却手段を装備し、上部と下部との間に邪魔板を配置した真空分離装置が開示されている。邪魔板を介して上部と下部とを所定の温度に設定し、加熱部からの熱輻射による凝固物の落下を防止しつつ塊状スポンジチタンから塩化マグネシウムと未反応の金属マグネシウムを分離するものである。また特公平5-21970号公報には、減圧状態に保った空間内でマグネシウム及び塩化マグネシウムを気化し、この蒸気を冷却面で凝固させることによりチタンなどの耐火金属からマグネシウム及び塩化マグネシウムを分離する方法において、マグネシウムの分圧が低下する分離工程後半期に、上記冷却面を追加拡張し、除去効果を向上させる方法が開示されている。

【0007】上記従来技術では、クロール法における分離工程において、分離する装置面での改良により分離の効率を向上させ、マグネシウム及び塩化マグネシウムを分離して生成した塊状スポンジチタンを精製している。これらの方法は生成した塊状スポンジチタンの周囲に存在する塩化マグネシウムや未反応の金属マグネシウムの分離除去においては効果を挙げているが、生成した塊状スポンジチタンの内部に存在する塩化マグネシウムや未反応の金属マグネシウムは、スポンジチタン中の網目状の細孔内部に残留してしまい、前記の分離装置あるいは分離方法では必ずしも十分に除去できないという問題があった。このように塊状スポンジチタン内部に塩化マグネシウムや未反応の金属マグネシウムが残留していること、高品質でかつ安定した品質の金属チタンが得られない。また、スポンジチタンはこれを溶解してチタン材として使用するが、塩化マグネシウムや金属マグネシウムが残留していること、例えば消耗電極法では溶解することは困難である。

【0008】

【発明が解決しようとする課題】上記のように、一方でチタン中の酸素成分を安定的に制御するチタンの製造方法、特に、電子ビーム溶解法で酸素含有量を制御したチタインゴットを製造する方法が望まれ、また他方でスポンジチタン中の残留塩化マグネシウムや金属マグネシウムを効率よく分離・除去し、高品位の安定した品質のチタンを製造する方法が望まれていた。

【0009】従って、本発明の課題は、チタン中の酸素含有量を安定して調整してチタンを製造する方法、特にチタン中の酸素含有量を安定して調整しかつスポンジチタン中の不純物の分離を効率よく行い、塩素やマグネシウム等の不純物が極めて少ない高品位でありかつ品質の安定したチタンを得るための製造方法を提供することに

ある。

【0010】

【課題を解決するための手段】かかる実情において、本発明者らは、上記課題について鋭意検討を重ねた結果、ある程度の粒径に調整したスポンジチタン顆粒と酸化チタン粉末を混合し減圧下で加熱処理した後、溶解することにより、チタン中の酸素含有量を安定して調整でき、しかもスポンジチタン顆粒が不純物を多く含むものであっても、チタン中の不純物を効率よく分離でき、塩素やマグネシウム等の不純物が極めて少ない高品位でありかつ品質の安定したチタンが得られることを見出し、本発明を完成するに至った。

【0011】特に前記分離操作後のスポンジチタンを顆粒の状態で減圧下で加熱処理することによりスポンジチタン中の残留不純物を効率よく分離できる。これは、スポンジチタンをそのまま容器内で減圧下で加熱処理する「分離」工程の後に続いて行うことから「再分離」工程と呼ばれる。また、処理効率を向上するために、分離操作後のスポンジチタンの選択された部分のみを顆粒の状態に減圧下で加熱処理することは「選択再分離」と呼ばれる。この「再分離」工程と酸化チタン粉末添加工程を組み合わせることにより有益な結果が得られる。再分離用の顆粒状のスポンジチタン粉末と酸化チタン粉末との混合物を加熱処理することによって、スポンジチタンの再分離と併せて、酸化チタン粉末をスポンジチタン表面に焼結させ、酸化チタン中の酸素をスポンジチタンに浸透させることができ、電子ビーム溶解などの方法で溶解した場合、酸化チタン粉末の飛散を防止することができると判明した。こうして、上述した再分離の困難さと添加した酸化チタンの溶解時の飛散という2つの問題を一挙に解決することができ、

【0012】すなわち、本発明のチタンの製造方法は、平均粒径1〜50mmのスポンジチタン粉末と酸化チタン粉末とを混合し、減圧下で加熱処理して、酸化チタン粉末粒子がスポンジチタン粉末粒子周囲に焼結した酸化チタン粉末焼結スポンジチタン粉末を生成した後、該酸化チタン粉末焼結スポンジチタン粉末を溶解して、酸素含有量を調整したチタンを製造することと特徴とする。

【0013】上記の通り、特に有益な態様として、前記スポンジチタン粉末が四塩化チタンを金属マグネシウムで還元して生成させた塊状スポンジチタンを平均粒径1〜50mmの顆粒に調整した再分離用スポンジチタン粉末であることを特徴とする上記のチタンの製造方法が提供される。

【0014】好ましくは、前記酸化チタン粉末に含まれるFe、Al、SiおよびNaが各々20ppm未満でありかつC1が500ppm未満であり、前記酸化チタン粉末粒子がスポンジチタン粉末粒子周囲に焼結した酸化チタン粉末焼結スポンジチタン粉末を容器内に充填し、次いで容器内をアルゴンガスに置換した後、真空雰

雰囲気下で加熱処理し、加熱処理の温度が600～1100℃にあり、そして溶解が電子ビーム溶解により実施される。

【0015】

【発明の実施の形態】本発明におけるスポンジタンは、再分離を特に必要としないスポンジタンおよび再分離を必要とするスポンジタン両方を対象とするが、再分離を必要とするスポンジタンを用いることが実益的である。

【0016】ここでは、後者を例にとって説明する。塊状のスポンジタンは、加熱炉内に設置された反応容器にマグネシウム(Mg)を入れ、不活性ガスを導入しながら900℃前後の温度に加熱し、そこに四塩化チタン(TiCl<sub>4</sub>)を滴下し、熔融金属マグネシウムで還元する所謂クロール法により生成させる。これにより、塊状のスポンジタンが生成される。そのパッチサイズは、設備規模、操業性等を考慮して、通常3トン/パッチ以上、好ましくは3～10トン/パッチである。反応容器内で塊状スポンジタンを生成させた後、副成する塩化マグネシウム(MgCl<sub>2</sub>)および未反応の金属マグネシウム蒸気を反応容器から抜き出す。好ましくは、塊状スポンジタンを容器から抜き出す前に、反応容器内を減圧、加熱し、生成塊状スポンジタン中の塩化マグネシウム等を蒸発させ、除去する工程(分離工程と呼ばれる)が実施される。分離工程条件は次の通りである：

真空中度： $10^{-2}$ ～ $10^{-4}$ Torr (通常 $10^{-3}$ Torr)

加熱温度：1000～1100℃ (通常1055℃)

加熱時間：パッチサイズによるが、50～10時間

分離工程は、塊状スポンジタンを収納する反応容器に塩化マグネシウム等の捕集・回収のため冷却凝縮器(反応容器と同等もしくは類似の容器を使用できる)を並置して連結部を介して連通状態とし、凝縮器の下部を減圧系統に接続して、凝縮器の外面を水冷することにより実施される。反応容器から抜き出された塩化マグネシウム蒸気等は水冷された凝縮器の内壁に凝結する。

【0017】その後、塊状スポンジタンを常温まで冷却し、反応容器底部から挿入したパッチにより押し上げ、反応容器上端から取り出し、それを作業盤上で解砕することによって、塊状スポンジタンを微細化し、平均粒径1～50mm、好ましくは3～25mm、より好ましくは4～19mmの顆粒に調整する。

【0018】前記微細化は、公知の方法により行うことができるが、通常塊状スポンジタンを大型プレス切断機である程度大きさの塊状物に切断し、次いでこの塊状物をジョークラッシャーあるいはダブロールクラッシャー等の破砕機または破砕整粒機により最終的に上記平均粒径の範囲に調整する。

【0019】前記微細化は通常大気中で行われるが、大

気中の水分がスポンジタン、スポンジタン中の塩化マグネシウムあるいは未反応のマグネシウムと接触し、スポンジタンが汚染される結果として、スポンジタン中の酸素含有量が増加する傾向がある。これを防ぐために、本発明では、前記微細化する雰囲気湿度をコントロールして行うことも可能であり、例えば雰囲気中の絶対湿度を $10\text{ g-H}_2\text{O/m}^3$ 以下で行う。具体的には、微細化を行う環境の湿度を、エアークンデショナーあるいは除湿機あるいは乾燥空気などで制御する。

【0020】塊状スポンジタンをより微細化したほうが、後の減圧下での加熱処理で不純物は除去し易いが、平均粒径を1mmより小さくすると、逆に空気中の塵素、水分あるいは酸素と接触しスポンジタンが酸素、酸素で汚染されてしまう。他方、平均粒径が50mmより大きい場合、後の減圧下での加熱処理の際、スポンジタンが焼結凝集してしまい、加熱処理を行った容器からスポンジタンを抜き出すことが困難となる。好ましくは3～25mm、より好ましくは4～19mmに整ずると、操作性が安定し、無効率である。そうした理由で、塊状スポンジタンは、平均粒径1～50mm範囲に微細化される。つまり、上記平均粒径の範囲に制御することにより、1) 塵素および酸素による汚染を最低限に抑え、2) 加熱処理の際、焼結による凝集を防ぎ、スポンジタンを加熱容器から取り出しやすくするという効果が得られる。尚、スポンジタンの最終製品の平均粒径は4～20mmであり、上記微細化の際、最終製品の粒径と同じ粒径に調整しておけば、加熱処理の後、再度解砕する必要がなくなり、工程が簡略化できる。

【0021】上述したように、塊状スポンジタンを微細化し、平均粒径1～50mmの顆粒に調整する過程において、先ず大型プレス切断機である程度大きさの塊状物に切断または解砕するが、この過程の後、塩化マグネシウムが含まれるスポンジタンの塊状物を選択・採取してこの後の微細化工程で、この選択採取した部分のみ平均粒径を1～50mmに調整することも可能である。塩化マグネシウムが含まれるスポンジタンの塊状物の選択方法としては、切断または解砕後のスポンジタン表面の色相を目視等により選択する方法、また一部スポンジタンをサンプリングしてその塩素含有率を測定し選択する方法が挙げられる。具体的には、四塩化チタンを金属マグネシウムで還元して生成させた3トン以上の塊状スポンジタンを切断し解砕して10～100kgの塊状物とし、塩素含有率0.5重量%以上の塊状物を選択する。このようにある程度大きさの塊状物を選択し、さらに解砕して平均粒径1～50mmの顆粒に調整する。本発明においては、製造されたスポンジタン全量、上記の選択・採取された部分、もしくは選択・採取された以外の残りの部分いずれをも微細化したスポンジタン粉末を対象とする。生成した



塊状スポンジチタンを減圧下で高温加熱することにより、そこから塩化マグネシウムと未反応の金属マグネシウムなどの不純物を蒸発させ分離・除去した後、解砕し、ある程度の粒径の顆粒に調整した後、全量もしくは不純物の多い部分を減圧下で加熱処理することにより（再分離）、不純物が効率的に分離除去でき、さらに解砕したことによる酸素等の汚染も抑えることができ、結果として酸素量または製造分の少ない高純度のスポンジチタンが効率よく製造できるものである。生成した塊状スポンジチタンは、塩化マグネシウムなどの不純物は、均一に分散しているわけではなく部分的に点在して含まれているため、上記のように不純物の含まれている比較的不純物の多い部分を選択・採取し、加熱処理を行う（選択再分離）ほうが効率的である。

【0022】次に本発明で用いられる酸化チタン粉末の粒径・比表面積などの粒子性状については、任意であるが、平均粒径は、好ましくは0.01～5μm、より好ましくは0.05～2μm、さらに好ましくは0.1～1μmであり、比表面積は、好ましくは0.5～100m<sup>2</sup>/g、より好ましくは1～50m<sup>2</sup>/g、さらに好ましくは2～30m<sup>2</sup>/gである。スポンジチタン粒子周囲に均一に分散させその後の加熱処理で焼結するという点においては、粒径の小さい酸化チタン粉末が好ましいが、あまり微粒でもその取扱いが難しく、上記のような平均粒径の範囲が好ましい。

【0023】さらに、本発明で用いられる酸化チタンは、不純物として酸化チタン粉末中に含まれるFe、Al、SiおよびNaが各々20ppm未満、望ましくは10ppm未満、さらに望ましくは5ppm未満である。また、酸化チタン粉末中のClは500ppm未満、望ましくは300ppm未満、さらに望ましくは100ppm未満である。

【0024】本発明で用いられる酸化チタンは種々の方法によって製造し得るが、例えば（1）硫酸チタン、硫酸チタンなどの含チタン溶液を加水分解させる方法、（2）チタンアルコキシドなどの有機チタン化合物を加水分解させる方法、（3）三塩化チタンあるいは四塩化チタンなどのハロゲン化チタン水溶液を中和又は加水分解させる方法、（4）四塩化チタンを気相中で酸素と接触させ酸化させる気相法、あるいは（5）焼結して水を生成する水素ガス等の可燃性ガスと酸素を燃焼バーナーに供給し火炎を形成し、この中に四塩化チタンを導入する火災加水分解法などの方法が挙げられる。このうち、乾式法が低コストで、しかも所望の粒子特性を有する酸化チタン粉末が得られる点で好ましい。これらの酸化チタンの製造方法のなかでも、より高純度の酸化チタンまた低コストの酸化チタンを得る方法としては、

（4）の気相法、あるいは（5）の火災加水分解法などの四塩化チタンを気相において酸化する方法（四塩化チタンの気相酸化法）が好ましく、液相法で得られる酸化

チタンのような不純物元素が混入した残留することがなく、酸化チタン以外の他成分を殆ど含まない高純度の酸化チタン粉末であるので、金属チタン中に他の不純物を混入させることなく、高品位のチタンを得ることができる。こうした酸化チタンは、本件出願人から製造販売されており、例えば東邦チタニウム株式会社製高純度酸化チタンNシリーズ、LSシリーズとして入手することができる。これらは電子分野に用いられ、上記不純物基準を満足する製品である。

【0025】次いで、上記の顆粒状のスポンジチタンと酸化チタン粉末を混合する。混合方法については、公知の粉体を混合する方法および装置が採用し得る。具体的にはロータリーミキサー、ラインミキサー、ナウターミキサーなどが挙げられる。また、顆粒状スポンジチタンと酸化チタン粉末を混合する際、両者を少量づつ分割あるいは連続して混合容器などに添加し混合することが望ましい。分割添加する場合、全重量を3回以上に分けて添加し混合することが望ましい。顆粒状スポンジチタンと酸化チタン粉末を一括して接触、混合した場合、スポンジチタン中に酸化チタン粉末が偏在し、最終的に溶解した後、チタン溶解品中の酸素分布のばらつきの原因となる。

【0026】上記のように顆粒状スポンジチタンと酸化チタン粉末を混合した後、該混合物を減圧下で加熱処理を行う。その際の条件は次の通りである：

真空度：10<sup>-2</sup>～10<sup>-4</sup>Torr（通常10<sup>-3</sup>Torr）

加熱温度：600～1100℃、好ましくは900～1050℃

加熱時間：10～100時間

【0027】このように、顆粒状スポンジチタンと酸化チタン粉末の混合物を減圧下で加熱処理することによって、酸化チタン粉末をスポンジチタン表面に焼結させ、酸化チタン中の酸素をスポンジチタンに浸透させることができる。先に説明したように、顆粒状スポンジチタンと酸化チタン粉末の混合物をそのまま、電子ビーム溶解などの方法で溶解した場合、酸化チタン粉末が溶解炉内で飛散してしまうが、本発明では、上記のように加熱処理によって酸化チタン粉末をスポンジチタン表面に焼結させるので、溶解中でも酸化チタン粉末が飛散することがない。従って、最終的な製品のチタンを所定の酸素含有量に制御する場合、このように溶解中のチタンの酸素がまったくないので、原料であるスポンジチタンの酸素含有量と成分調整する最終製品の酸素含有量にあわせて酸化チタン粉末を混合すればよく、ばらつきがなく安定して酸素含有量の制御が可能である。併せて顆粒状チタン粉末の（選択）再分離が進行する。

【0028】上記のように減圧下で加熱処理する前に、顆粒状スポンジチタンと酸化チタン粉末の混合物を加熱容器に投入するが、そのままだでは空気雰囲気であり、加

熱処理した際、空気中の酸素および窒素でスポンジチタンが汚染されるため、投入後、容器内をアルゴンガスで置換することが望ましい。さらに、スポンジチタンおよび加熱容器中の水分を除去するため、上記加熱処理の前に300〜500℃程度の低温で処理することも好ましい態様の一つである。

【0029】上記加熱処理する際、図1に示すように、再分離用スポンジチタン顆粒および酸化チタン粉末を収納する加熱容器1と、スポンジチタン顆粒から蒸発分離された塩化マグネシウムなどの不純物をトラップする塩化マグネシウム回収冷却凝縮器2とから構成される。加熱容器1は内面にヒータ3を備える加熱炉4内に設置される。加熱容器1の蓋体は連結管5により塩化マグネシウム回収冷却凝縮器2に連結されている。冷却凝縮器2の底部は真空ポンプにつながる排気系統6に接続され、そしてその外壁は、冷却用のシャワー水を散布する冷却手段7により冷却されるようになっている。前記加熱容器の材質はステンレス鋼、炭素鋼、または外側がステンレス鋼で内側が炭素鋼あるいはチタンとしたグラッド鋼が用いられる。通常、該加熱容器は、四塩化チタンと金属マグネシウムを還元して塊状スポンジチタンを生成させた反応容器をそのまま用いることができる。また、この冷却凝縮器も、塊状スポンジチタン生成後の前記分離工程時のものを使用することができる。

【0030】また、上記のような既存の装置のほか、図2に示すように、本発明の方法に用いられる酸化チタンの添加焼結と併せて、再分離を行う真空分離装置10として加熱容器1上端の蓋体にフラジにより簡易に着脱可能でありそして冷却器を具備しつつ蒸発した不純物を効率的に捕集できる分離装置を用いることができる。加熱容器1は、再分離用スポンジチタン顆粒および酸化チタン粉末を収納する。真空分離装置は、冷却媒体を流通させるための冷却ジャケット11及び真空ポンプへ連結された吸引口12を有する冷却器13と、開口部を介して前記容器と連通する受け器14とを備え、前記冷却器は前記蓋体の前記加熱容器の外部にそして前記受け器は前記加熱容器の内部に設置され、前記冷却器と前記受け器を接続管15で連結した構成とする分離装置である。このような真空分離装置では、容器の内部に開口部を有する受け器を備えているため、再分離によって蒸発し、冷却器によって凝縮、析出した固体状あるいは液状の塩化マグネシウム等が受け器に回収され、加熱容器に戻らないような構造となっている。さらに、前記受け器には、前記加熱容器と連通する開口部より下部を遮熱板が配設するように構成されている。この遮熱板により、析出したものが、再度、気化することが防止され、塩化マグネシウム等の回収効率を高めることが可能となる。

【0031】このように、加熱容器に取り付けられて、冷却器と受け器を接続した着脱式の分離装置を用いることによって、容積効率を高めることが可能とな

り、酸化チタンの添加・焼結と併せて、効率的にそして簡便に再分離を行い、より純度の高いスポンジチタンとそこに焼結した酸化チタン混合物を製造することができる。しかも、本来の分離設備が再分離の処理から解放されて独立した操業を実施できることになり、分離工程における処理能力の低下を防止でき、結果としてスポンジチタンの生産効率を向上することが可能となる。この分離装置における冷却器の内容積は通常加熱容器の内容積の30%以下であり、好ましくは2〜10%である。従来の分離装置は、加熱容器と冷却器の容積比がほぼ1:1であり(図1参照)、非常に大きい冷却能力を必要としていたが、このような分離装置では冷却器の容積が小さいため、効率よく冷却し、再分離と酸化チタンの添加焼結を好適に行うことが可能である。生成されたスポンジチタンのうち、不純物の再分離を特に必要とする部分のみを容積効率の高いしかも着脱式の凝縮冷却装置を使用して実施することにより最小限の冷却能力で最大限の分離効果をおげることが可能となる。全量処理の場合より、その分離効果は格段に高くなり、操業性は大幅に向上する。酸素含有量を変えた多品種のチタンを少量ずつ簡便迅速に製造することができる。

【0032】以上のように、減圧下での加熱処理した顆粒状スポンジチタンと酸化チタン粉末の焼結混合物は、常温で冷却し加熱容器から取り出す。その後、必要に応じて解砕される。

【0033】次いで、加熱処理した顆粒状スポンジチタンと酸化チタン粉末の焼結混合物を溶解して最終的にチタンを得るが、溶解方法としては電子ビーム溶解あるいは真空アーク溶解などの方法が採用でき、本発明ではブリケットやロッドに溶解原料を成形する必要のないペース溶解による電子ビーム溶解においてチタンインゴットを製造するのに特に効果的である。酸化チタン粒子はスポンジチタン粒子周囲に焼結されているので、最初に述べた溶解に際しての酸化チタンの飛散の問題は排除される。

#### 【0034】

【実施例】以下、本発明を実施例および比較例によりさらに具体的に説明する。

(実施例)還元反応容器内において四塩化チタンと溶融金属マグネシウムを還元反応し、8トンの塊状スポンジチタンを生成させた。その後、溶融塩化マグネシウムおよび未反応の溶融金属マグネシウム蒸気を抜き出し、その後1.0<sup>-3</sup>Torrの減圧下、1055℃で80時間加熱処理を行い更に不純物を分離した。塊状スポンジチタンを還元反応容器から抜き出し、切断機にて約10kgの塊状に切斷および解砕し、塩化マグネシウム含有量の多い塊状スポンジチタンのみを選択・採取した。その後、この選択・採取部分をジョークラッシャーにて解砕し平均粒径4〜19mmの顆粒に調整した。

【0035】この顆粒状スポンジチタン2500kgと

平均粒径15 $\mu$ mの酸化チタン粉末40kgを3回に分けてラインミキサーに装入して、10分間混合した。尚、酸化チタン粉末としては、NS90（平均粒径10～15 $\mu$ m）を使用した。このようにして得られた顆粒状スポンジチタンと酸化チタン粉末の混合物を、前記図1に示したような冷却凝縮装置を取り付けた加熱容器に充填した。その後、加熱容器内をアルゴンガスで置換し、次いで減圧下で400℃まで加熱し、50時間経過後再度アルゴンガスを装入した。その後、加熱容器内及び冷却凝縮装置内を減圧にし、700℃で2時間、800℃で2時間、900℃で2時間、最後に1000℃に昇温し40時間減圧下での加熱処理を行った。加熱処理終了後、常温まで冷却した後、容器内の酸化チタン焼結スポンジチタン粉末塊を抜き出し解砕した。このスポンジチタン中の塩素含有量を電位差滴定法により測定し、その結果を表1に示した。

【0036】その後この酸化チタン焼結スポンジチタン147kgを電子ビーム溶解にて、電子ビーム出力40

0kW、平均溶解速度800～900kg/時間で溶解し、長さ2700mm、660mm×1350mm矩形断面の角形チタンインゴットを作製した。得られた、チタンインゴット中のトップ、ミドルおよびボトム（ここでトップはインゴット上端から下部に向かう300mmの部分、ミドルはインゴットの中間部分、ボトムはインゴットの下端から上部に向かう300mmの部分）の3箇所のサンプルを採取し、それぞれの酸素含有量を（測定方法）により測定し、インゴット内での酸素含有量のばらつきを評価した。さらに、上記のチタンインゴットの製造を3バッチ行い、各チタンインゴットの平均酸素含有量を測定した。これらの結果を表1に示した。

【0037】（比較例）実施例1において、顆粒状スポンジチタンと酸化チタン粉末を混合した後、減圧下で加熱処理しなかった以外は実施例1と同様に行った。この結果を表1に示した。

【0038】

【表1】

		実施例	比較例
スポンジチタン中の塩素含有率 (重量%)		0.07	0.51
目標酸素含有量(重量%)		0.0675	0.0675
同一インゴット 内の3箇所の 酸素分析結果	平均酸素含有量 (重量%)	0.0650	0.0550
	標準偏差	0.0006	0.0140
3バッチの インゴットの 酸素分析結果	平均酸素含有量 (重量%)	0.0670	0.0525
	標準偏差	0.0034	0.0128

【0039】

【発明の効果】以上のように、本発明では、平均粒径1～50mmの粒径に調整したスポンジチタンと酸化チタン粉末を混合し減圧下で加熱処理した後、溶解することにより、チタン中の酸素含有量を安定して調整でき、かつスポンジチタン中の不純物を効率よく分離でき、塩素やマグネシウム等の不純物が極めて少ない高品位でありかつ品質の安定したチタンが得られる。再分離と酸化チタンの添加焼結を好適に行うことが可能である。溶解時の酸化チタンの飛散の問題が生じない。酸素含有量を変えた多品種のチタンを所望量づつ簡便迅速に製造することができる。

【図面の簡単な説明】

【図1】加熱容器および冷却凝縮装置の構成図である。

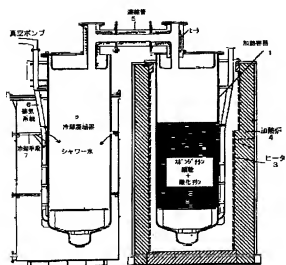
【図2】着脱式の別の冷却凝縮装置を備えた加熱容器を示す構成図である。

【図3】従来の酸化チタンを添加してスポンジチタンの溶解を行う電子ビーム溶解装置の概略斜視図である。

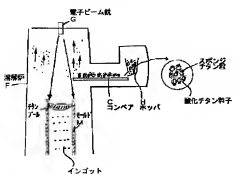
【符号の説明】

- 1 加熱容器
- 2 冷却凝縮器
- 3 ヒータ
- 4 加熱炉
- 5 連結管
- 6 排気系統
- 7 冷却手段
- 10 真空分離装置
- 11 冷却ジャケット
- 12 吸引口
- 13 冷却器
- 14 受け器
- 15 接続管

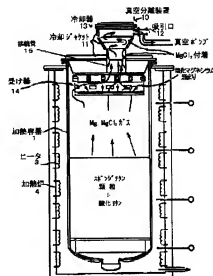
【図1】



【図3】



【図2】



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Patent Application Publication No. 31-

Patent Application Publication Date: September 8, 1956  
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(Total of 3 Pages)

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A Method For Continuously Manufacturing a Metal Titanium

Brief Explanation of the Drawings

The figure is a vertical cross-sectional view of a working example of the present invention.

Detailed Description of the Invention

The present invention relates to a method for continuously manufacturing a metal titanium in which a liquid alkali metal or alkali rare earth metal, alone or in a mixture of two or more, is injected along with liquid titanium tetrachloride into a reaction chamber from a nozzle at a relatively low temperature, a reduction reaction is conducted at a low temperature between 700°C and 900°C, which is above the melting point of the chloride reductant, using only the heat from the reaction, the titanium mixture is

collected in slurry form containing molten salts, a tap device is heated or cooled to transfer the product to a vacuum heat furnace, and vacuum distillation is performed.

In the present invention, a liquid alkali metal or alkali rare earth metal, alone or in a mixture of two or more, is injected along with liquid titanium tetrachloride and an inert gas such as argon if desired from a concentric double nozzle in spray or stream form into a reaction chamber purged with an inert gas such as argon, and a reduction reaction is performed.

The melting points of the alloy metal reductants are shown in the following table.

Melting Points

	Mg	Ca	Na	K
Alone	650°C	850°C	97.5°C	63.5°C
Alloys	Na-K Alloys (Liquid at Temperatures Below 50°C) Na 3 ~ 75%			
	Ca-Mg Alloys (Liquid at Temperatures Below 500°C) Ca 75 ~ 82%			
	Ca-Mg Alloys (Liquid at Temperatures Below 600°C) Ca 8 ~ 23% or 70 ~ 85%			

The Na obtained by direct electrolysis of table salt contains Ca 1% and has a melting point around 150°C.

This can be introduced into the reaction chamber at a temperature between room temperature and 600°C. The heat from the introduction of an alloy containing a substantial amount of an alkali metal or alkali earth metal at 500°C or more initiates the reaction. The heat from the reaction then maintains the temperature inside the reaction chamber between 700°C and 900°C, which is above the melting point of the chloride reductant. The temperature is then lowered to between 700°C and 800°C to extract the

metal titanium and molten salt mixture produced by the reaction. Because of the difference in specific gravity, the metal titanium precipitates out of the molten salts. The molten salt supernatant is then removed, and the metal titanium slurry on the bottom is extracted. The metal titanium is discharged to a vacuum heat furnace heated by a tap device and the temperature inside the vacuum furnace is raised to between 1200°C and 1300°C. The unreacted salts are evaporated, and the metal titanium is condensed and removed. Metal titanium can be continuously manufactured using a reduction reaction and extracted by switching between two vacuum furnaces.

In the present invention, the titanium tetrachloride and metal reductant used to produce the metal titanium in the reaction can be supplied to the reaction chamber at a low temperature. The natural heat from the molten metal spray initiates the reaction. The heat from the reaction itself then serves as the source of heat for the reaction. The temperature can be adjusted by changing the amount of reaction materials injected into the reaction chamber. Because the metal titanium produced by the reaction is extracted in slurry form mixed with molten salts, it is easy to handle. A metal titanium with a high degree of purity can be manufactured easily and economically. It can also be manufactured continuously because none of the materials contaminate the walls of the chamber.

The following is an explanation of the method of the present invention with reference to the drawing.

In this method, a heat-resistant metal or metal alloy such as a stainless steel-titanium alloy is added to a metal titanium reduction furnace 2 that has sidewalls 1 that expand

from the top towards the middle 3 and then narrow towards the bottom 4. The expanded middle keeps the temperature of the reaction product from dropping much and the bottom collects the reaction product and the molten salts while keeping the temperature constant. Liquid (or gaseous) titanium tetrachloride is injected from a concentric double nozzle 5, 5 with the liquid reductant. The tube 6 in the middle 3 of the reaction chamber is used to adjust the pressure inside the reaction chamber and purge the atmosphere inside the reaction chamber. The top hole 7 is used to extract the molten salts, and the tap device 8 is used to remove the titanium slurry precipitate. The heating and cooling of the precipitate by the tap device starts and stops the introduction of the precipitate into the vacuum heating furnace 9. This furnace is attached to the bottom 10 of the reaction furnace by a support means, and is made of a material that does not react with the product from the reaction furnace and is pressure-resistant so as to allow the gas pressure inside the furnace to be adjusted.

The titanium tetrachloride and a sodium-potassium (Na 50%) alloy are injected into the 50-l reduction furnace via the nozzle in the cylindrical top section. The atmosphere inside the reaction chamber is purged with argon gas from the tube 6. The 500°C titanium tetrachloride and molten sodium-potassium alloy spray provides natural heat. The amount is adjusted so that the natural heat coupled with the heat from the reduction reaction keeps the temperature inside the reaction temperature around 900°C. A slurry of molten salts and titanium powder is collected at the bottom of the reaction chamber. The metal titanium precipitate is introduced to the vacuum heat furnace beneath the reaction chamber via a stainless steel tap tube heated to 800°C. When the tap tube is cooled with water, the salts in the tube solidify and stop the flow of the reaction product into the vacuum heat furnace. When the vacuum heat furnace



is heated to between 1200°C and 1300°C, the residual sodium chloride and potassium chloride evaporate and pass through the discharge tube 11 to the salt solidifying device. At the same time, the vacuum heat furnace is cooled and the metal titanium is solidified and extracted. About 172 g of titanium is obtained from 800 g of titanium tetrachloride and 530 g of sodium-potassium alloy. Two vacuum heat furnaces can be used intermittently as part of a continuous manufacturing process.

### Claims

As explained in the specification and the drawing, the present invention is a method for continuously manufacturing metal titanium in which titanium tetrachloride and a reductant are injected into a reaction chamber with an inert atmosphere to produce metal titanium and salts, wherein a liquid alkali metal or alkali rare earth metal, alone or in a mixture of two or more, is injected along with liquid titanium tetrachloride into a reaction chamber from a concentric nozzle at a temperature between room temperature and 700°C, a reduction reaction is conducted at a temperature between 700°C and 900°C, which is above the melting point of the chloride reductant, using only the heat from the reaction, the metal titanium and molten salts are collected in slurry form, a tap device is heated or cooled to transfer the product to a vacuum heat furnace, and vacuum distillation is performed.



## 特 許 公 報

昭31-7808

公告 昭 31.9.8

出 願 昭 29.11.13

特 願 昭 29-24580

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(全3頁)

## 連続的に金属チタニウムを製造する方法

図面に示すものは本発明実施の一態様を例示した縦断面図である。

## 発明の詳細なる説明

本発明はアルカリ金属或はアルカリ土金属の単味又は混合物の液体を常温又は比較的低温に於て四塩化チタニウムの液体或は蒸気と共にノズルより同時に反応室へ噴射し、その反応熱のみにより還元剤の塩化物の融点以上の約700℃～900℃の低温で還元反応を行はしめ、スライム状で生成した塩とチタニウムの混合物を鋳融塩下へ収集し、タップ装置を加熱又は冷却することにより之を真空加熱炉へ移し真空蒸溜に附することを特徴とする連続的金属チタニウムの製法に係るものである。

即ち本発明に於ては、アルカリ金属或はアルカリ土金属の単味又は混合物を液体として四塩化チタニウムの液体或は蒸気にアルゴン混じり又は混じらないで同心二重管のノズルを通じ同時にアルゴン等の不活性ガス気流の反応室に霧状乃至瓦斯状として噴込み還元反応を起さしめるのであるが、之の場合金属還元剤の融点は下表の通りであるから、

融 点	Mg	Ca	Na	K
単 味	650℃	850℃	97.5℃	63.5℃
合 金	Na-K合金 (50℃以下で液体である合金の範囲) Na 3-75%			
	Ca-Mg合金 (500℃以下で液体である合金の範囲) Ca 75-82%			
	(600℃以下で液体である合金の範囲) Ca 75-82%			
	Ca 70-85%			

尚合金の直接電解で得られるNaはCaより前夜を含有するがこの融点は150℃附近である。

之等は常温乃至600℃以下の温度で反応室へ導入することが出来るし又反応開始はアルカリ金属或はアルカリ土金属を多く含む合金を500℃以上に加熱して導入することにより自然着火せしめ、尔後その反応熱により反応室内の温度は還元剤の塩化物の融点以上の700℃～900℃附近に保持する。この反応によつて生成された金属チタニウムと鋳融状態の塩或は混合塩を700℃～800℃程度に保持された収集部へ落下せしめ夫々の比重差によつて金属チタニウムと塩の混合物を鋳融塩の底へ沈澱せしめる。斯くして収集部へ溜つた鋳融塩とその底に貯つたスライム状の金属チタニウムを各取出口より取出す。その際金属チタニウムはタップ装置の加熱により真空加熱炉の中に流出させ更に之の真空加熱炉を1200℃～1300℃に加熱して塩及未反応の金属を蒸発除去し、粉末金属チタニウムのみを凝集採取するものであるが、前記真空加熱炉を他に用意されたものと交互に取替へて還元反応を中絶することなく連続的に金属チタニウムを生成し且採取するものである。

従つて本発明によれば、金属チタニウムの生成反応を行はしめるに当り反応物質である金属還元剤並に四塩化チタニウムを極めて低い温度で反応室へ供給することが出来るし、反応開始は鋳融金属の噴射による自然着火により行はれ且尔後の反応に必要とされる熱源は反応熱のみを利用すれば足り而もその温度の調節は反応物質の噴射量を調節することにより自由に調整出来、更に生成された金属チタニウムは鋳融塩中に混じスライム状で鋳融塩下に貯溜されるので之が取扱いも容易である限りでなく反応室内盤より異物の混入も防ぎ得る等連続的に純度の高い金属チタニウムを容易且経済的に製造することが出来るのである。

次に本発明の方法を図面について説明する。  
先づ本方法に於て使用する金属チタン還元剤の

一般様に付きその概要を述べれば耐熱性を有する金属又は合金例へばステンレス、チタン或はチタン合金等にて炉壁1を作り炉の上部を反応室2とし中央部は反応生成物の落下速度を小ならしめるため炉腹3を狭げ下部は反応生成物の塩と熔融状態に保つために保温されている炉底部4は反応生成物が収集される様に炉幅を狭くする。炉頂より四塩化チタニウムの液体(又は蒸気)を還元剤の液体と共に同時に噴射する同心円筒状のノズル5、5を設け、炉腹部3に炉内の圧力の調節及気固の置換のため管6を取付ける。炉下部には熔融塩を取出すタップホール7とスポンジチタンの泥状沈澱を取出すタップ装置8を取付けこのタップ装置は導管の加熱又は冷却によつて沈澱物の真空加熱炉9への導入を始めてり止めたりする。之の炉全体を支持装置を兼ねた鋼製の殻10に入れ炉内のガス圧と該殻内のガス圧を平衡させることにより還元炉材質の耐酸化、耐圧性を保たしめるものである。

還元炉内容積50lポンベ状の炉体頂部に四塩化チタニウムとナトリウム-カリウム合金(Na50%)とを噴出するノズルを設け炉内の気固を管6を以てアルゴンガスに置換した後、先づ四塩化チタニウムを霧状に噴射し次で500℃に加熱熔融された金属ナトリウム-カリウム合金を吹き込み自然着火させ炉内温度を900℃附近に保持する様に噴出量を調整して還元反応を続行し炉底部に熔融塩と粉状チタニウムとの混合物をスライム状で熔融塩下に収集せしめ800℃まで加熱したステンレスのタ

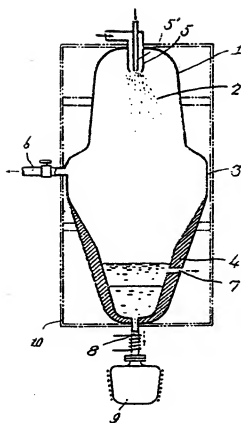
ップ導管を通じてスライム状態のまま下部の真空加熱炉に導き、次いでタップ導管を水冷して導管中の塩を凝固せしめ反応生成物の流入を中止せしめる。次に真空加熱炉に於て1200℃~1300℃に加熱して熔融塩として残置している塩化ナトリウム及塩化カリウムを蒸発させ之を排気管11を経て凝縮装置に導き同時に炉内のスポンジチタンを凝集安定せしめ、次いで真空加熱炉を冷却して金属チタニウムを取出す。之の間に使用した四塩化チタニウム800g、ナトリウム-カリウム合金530gに對し得られたチタンスポンジは172gである。尚真空加熱炉は順次交互に使用して連続的に反応は継続せしめるものである。

#### 特 許 請 求 の 範 囲

本文に詳記し且つ図面に示すように、不活性ガス気固の反応室内へ四塩化チタニウムと還元剤とを吹込んで反応させ、金属チタニウムと塩とを生成して金属チタニウムを製造する方法に於て液体状態のアルカリ金属或はアルカリ土金属の単味若しくは混合物を常温乃至700℃に加熱したものと四塩化チタニウムの液体或は蒸気とを同心円筒状のノズルより同時に反応室へ噴射して自然着火せしめその反応熱のみにより反応室内の温度を還元剤の塩化物の融点以上の700℃~900℃に保持し生成したチタニウムと塩との混合物をスライム状で熔融塩下へ集収し、タップ装置を加熱又は冷却することによりこれを真空加熱炉へ移し真空蒸溜を施すことを特徴とする連続的に金属チタニウムを製造する方法。

(3)

特許出願公告  
昭31-7808



In the present invention, the reactions of reduction are carried out by injecting, as a nebulosus or gaseous state, a liquid of an alkaline metal or an alkaline earth metal or a mixture thereof simultaneously with a liquid or vapor of titanium tetrachloride mixed with or without argon into a vapor zone of inactive gas such as argon in the reaction chamber through a nozzle composed of coaxial double tubes. In that case, since the reducing agents for metals have melting points listed below, they can be introduced into the reaction chamber at a temperature ranging from normal temperature to 600 °C.

Melting point

	Mg	Ca	Na	K
Metal mp.	650	850	97.5	63.5

Allôy Na·K alloy

(Range of alloys being a liquid at a temperature of 50° C and below)

Na 3~75 %

Ca·Mg alloy

(Range of alloys being a liquid at a temperature of 500° C and below)

Ca 75~82 %

(Range of alloys being a liquid at a temperature of 600° C and below)

Ca 8~23 %

Ca 70~85 %

Note: Sodium produced by direct electrolysis of sodium chloride contains approximately 1 % of Ca, and its melting point is about 150 ° C.

Further, the reduction reactions may be initiated by introducing an alloy (into the chamber) to cause them self-activation, said alloy containing a large quantity of the alkaline metal or alkaline earth metal and being heated to a temperature of 500 °C and above. Then, the temperature in the chamber is maintained by their reaction heats to a temperature of about 700 to 900 °C, which is higher than the melting point of the chloride of reducing agent. Then, titanium metal and molten salt or mixed salts produced by the above reactions are allowed to fall in a collecting portion kept at about 700 to 800 °C, and the mixtures of titanium metal and the salts are allowed to respectively precipitate to the bottom of the molten salt due to difference in specific gravity. The molten salt thus precipitated in the collecting portion and titanium metal precipitated below the molten salt in the slime form are taken out through respective outlets.

In that case, titanium metal is produced by introducing the titanium metal into a vacuum furnace by heating a tapping device, heating the vacuum furnace to 1200 to 1300 °C to remove the salt and nonreacted metal by vaporization, and then collecting powdered titanium metal only after its agglutination. By alternately replacing the vacuum furnace with another one, it is possible to continuously produce titanium metal without interruption of reduction reactions.

According to the present invention, therefore, it is possible to supply reactants of the metal-reducing agent and titanium tetrachloride to a reaction chamber at extremely low temperatures when carrying out reactions for production of titanium metal. The initiation of reactions is carried out by self-ignition caused by injection of molten metal. Also, it is sufficient to use the reaction heats as a heat source required for reactions. In addition, the temperature control can be done freely by controlling the injection quantity of the reaction materials. Also, since the produced titanium metal is mixed with the molten salt and stored in the form of slime below the molten salt, it is easy to handle the products as well as to prevent foreign matters of internal wall of the reaction chamber from getting into the reaction products.



Thus, the present invention makes it possible to easily and economically achieve continuous production of titanium metal with high purity.

The method of the present invention will be explained below with reference to the accompanying drawing.

Firstly, one embodiment of the titanium metal reduction furnace used in the process of the present invention will be outlined below. A furnace wall 1 is made of a heat-resisting metal or alloy such as stainless steel, titanium or titanium alloy. The furnace includes a reaction chamber 2 located at an upper portion, an enlarged furnace bosh 3 located at a middle portion, and a furnace bottom portion 4 kept its temperature constant to keep salts of reaction products in a molten state and tapered toward the bottom to collect reaction products therein. The furnace is provided at its top with a coaxial double tubular nozzle 5, 5' for concurrently injecting a liquid (or vapor) of titanium tetrachloride and a liquid of the reducing agent into the chamber from the top of the furnace. The furnace is also provided at the furnace bosh 3 with a pipe 6 for control of the internal pressure of the furnace and for replacement of atmospheres in the vapor zone.

The furnace is provided at its lower portion with a tapping hole 7 for taking out the molten salts, and a tapping device 8 for taking out the slurry of precipitated spongy titanium. The tapping device 8 allows the precipitate to start or stop the flow entering into a vacuum heating furnace 9 by heating or cooling a conduit connected thereto.

The furnace is wholly housed in a steel shell 10 serving as a supporting device and its internal gas pressure is equilibrated with that of the shell 10 to allow the furnace material to hold oxidation resistance and pressure resistance.

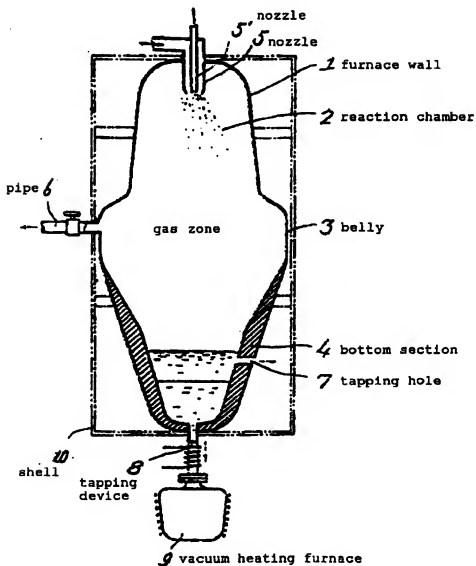
The nozzle for injecting titanium tetrachloride and a sodium-potassium alloy (Na 50%) is provided on the top of the furnace body like a bomb with an internal volume of 50 liters, the atmosphere in the furnace is replaced with argon gas through the pipe 6. Then, the reduction reaction is carried out by injecting titanium tetrachloride first by spraying and then injecting the molten sodium-potassium alloy heated to 500 ° C to ignite the furnace by itself, and controlling the injection quantities so as to keep the internal temperature of the furnace to the vicinity of 900 ° C.

By continuing the reduction reaction, a mixture of molten salts and powdered titanium in the form of slime is collected below the molten salt in the bottom portion of the furnace, and introduced into the underneath vacuum heating furnace through the tapping conduit as it is. Then, the inflow of the reaction products is stopped by cooling the tapping conduit with water to solidify the salt flowing through the conduit. In the vacuum furnace, the reaction products are heated to 1200 to 1300 ° C to evaporate the sodium chloride and potassium chloride remained therein as the molten salts, which are then introduced into a condensing device through a pipe 11. Simultaneously therewith, sponge titanium is agglutinated and stabilized. Then, titanium metal is taken out by cooling the vacuum furnace. Use of 800 g of titanium chloride and 530 g of sodium-potassium alloy yielded 172 g of sponge titanium. By using plural vacuum furnaces and replacing the vacuum furnace with another one, the reaction is carried out continuously.

## Claim:

A process for continuously producing titanium by introducing titanium tetrachloride and a reducing agent into an inactive gas zone in a reaction chamber to react them with each other so as to produce titanium and a salt, said process comprising the steps of concurrently injecting an alkaline metal or an alkaline earth metal in a liquid phase or a mixture thereof, heated to a temperature of from a normal temperature to 700° C, and titanium tetrachloride in a liquid or vapor phase from a coaxial tubular nozzle into the reaction chamber to cause spontaneous ignition; maintaining the temperature in the reaction chamber at a temperature of substantially 700 to 900° C not lower than the melting point of the chloride of the reacting agent by using only the reaction heat of the reduction; collecting a mixture of the titanium and the salt produced in the form of slime in a lower side under the melted salt; and heating or cooling a tapping device to thereby transfer the mixture to a vacuum heating furnace so as to be subjected to vacuum distillation.

## metal titanium -reducing furnace



Cited Reference 1

(JP-B S31-007808)

What is claimed is:

A process for continuously producing titanium by introducing titanium tetrachloride and a reducing agent into an inactive gas zone in a reaction chamber to react them with each other so as to produce titanium and a salt, said process comprising the steps of concurrently injecting an alkaline metal or an alkaline earth metal in a liquid phase or a mixture thereof, heated to a temperature of from a normal temperature to 700°C, and titanium tetrachloride in a liquid or vapor phase from coaxial tubular nozzles into the reaction chamber to cause spontaneous ignition; maintaining the temperature in the reaction chamber at a temperature of substantially 700 to 900°C not lower than the melting point of the chloride of the reacting agent by using only the reaction heat of the reduction; collecting a mixture of the titanium and the salt produced in the form of slime in a lower side under the melted salt; and heating or cooling a tapping device to thereby transfer the mixture to a vacuum heating furnace so as to be subjected to vacuum distillation.

Cited Reference 3

(JP-A S49-042518/1974)

What is claimed is:

A process for producing titanium tetrachloride by supplying a raw titanium material and a reducing substance to a fluidized chlorinating furnace and introducing a chlorine-containing gas to chlorinate the raw titanium material at a temperature of 900 to 1100°C while being fluidized, characterized in that the chlorine-containing gas is introduced so that the superficial linear velocity of the gas in the furnace (based on the reaction temperature) becomes 5 to 20 cm/sec., and that the amount of the chlorine-containing gas is increased so that the superficial linear velocity of the gas can intermittently achieve a value 1.2 to 3 times larger than said superficial linear velocity (5 to 20 cm/sec.).

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001185131

WPI Acc No: 1974-58991V/197433

Titanium tetrachloride fluid bed prodn - the loss of material reduced by lowering the linear velocity of reactive gases

Patent Assignee: ISHIHARA SANGYO KAISHA LTD (ISHH )

Number of Countries: 001 Number of Patents: 001

Patent Family:

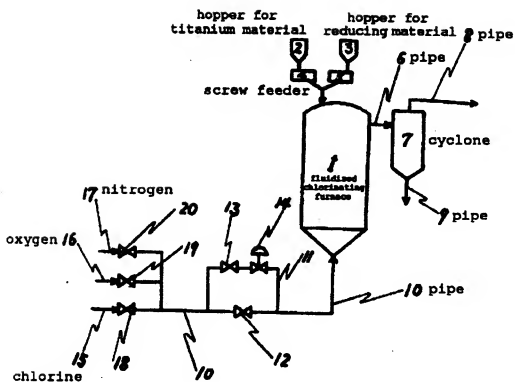
Patent No	Kind	Date	Applicat No	Kind	Date	Week
JP 49042518	A	19740422				197433 B

Priority Applications (No Type Date): JP 7286673 A 19720831

Abstract (Basic): JP 49042518 A

Fluidized Ti-contg. material and C are treated in a furnace with Cl-contg. gas (linear velocity 5-20 cm/sec.) at 900-1000 degrees C. The velocity is gradually increased to 1.2-3-fold. In an example, Ti material 32-200 mesh >99% contg. TiO<sub>2</sub> 96.3 and Fe<sub>2</sub>O<sub>3</sub> 14% 28.0 and petr. coke 20-80 mesh >99% contg. 96-98% C 6.5 kg/hr. were introduced into a 40 diam. x 150 cm cylinder and treated with 1/min Cl 197, O<sub>2</sub> 220, and N<sub>2</sub> 35 at 15.6 cm/sec velocity and 328, 34, and 59 at 25.9, resp., for 8 and 2 min, resp. Carry-over of the Ti material was 2.5% and 5.2% resp.  
Derwent Class: M25





(2000円)

# 特 許 願

昭和47年 8月31日

特許庁長官 三 宅 英 殿

1. 発明の名称 **四酸化チタンの製造方法**
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## 5. 添付書類の目録

- (1) 願書 1 通
- (2) 明細書 1 通
- (3) 図面 1 通
- (4) 参考資料 1 通

47 056673

明 細 書

## 1. 発明の名称 四酸化チタンの製造方法

### 2. 特許請求の範囲

焼結酸化チタン原料及び還元性物質を供給し、還元含有ガスを導入して、900～1100℃で焼結還元して四酸化チタンを製造する方法において、炉内のガスの空塔流速（反応温度基準）が5～20m/秒となるように還元含有ガスを導入し、かつ同程度の空塔流速が反応温度の1.2～3倍の焼結炉内の値となるように還元含有ガス導入量を増加させることを特徴とする四酸化チタンの製造方法。

### 3. 発明の詳細な説明

含チタン原料を焼結還元して四酸化チタンを製造する方法においては、チタン原料及び還元剤を供給し、炉内に適量空塔流速約20m/秒程度以上の流速で還元含有ガスを上向きに吹込んで、焼結層を形成させながら反応をおこなわせる。この方法では、生成する四酸化チ

⑬ 日本国特許庁

# 公開特許公報

⑪特開昭 49-42518

⑬公開日 昭49.(1974) 4.22

⑫特願昭 47-86673

⑭出願日 昭47.(1972) 8.31

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庁内整理番号 ⑮日本分類

7225 42 10 E11  
7203 41 15 E2

タンを含む還元性ガスが酸化炉上部から吹き出されるときに、一部の含チタン原料が未反応のまま生成還元性ガスに伴われて焼結炉からキャリーオーバーすることが避けにくく、工業的実用上問題となっている。

このキャリーオーバー現象をできるだけ少なくするためには、使用する含チタン原料は粒度分布の巾が小さく、粒度および密度が焼結炉内での空塔流速がかなりものであることが要求される。現在一般に使用されている天然ルナル鉱石は、それ自体焼結炉内での空塔流速が適当であるが、それでも反応進行に伴う粒度変化などもあって、キャリーオーバーの問題を完全に回避することはむづかしい。最近、天然ルナル鉱石の焼結に伴って、産出量の多い含チタン鉱石中のチタン分を富化し天然ルナル鉱に近い組成のチタン焼結物を得て、これを代替使用する試みが行われているが、この場合はキャリーオーバー抑制は更にやつかりな問題となる。例えば含チタン焼結物を焼結して使用用途に供するまでの不純物

を除去して得られるナタン炭化物は、通常炭酸化反応用原料として適さない炭粉状のもの、或は粗粒であつても比重が小さかつたり、反応工までの取手の消滅や腐蝕のために炭粉化したりして、キャリアー吸着を防ぐことがむづかしいものが多い。また、含ナタン炭化物中の炭分を選択的に炭酸化して除去することによつて得られるナタン炭化物も同様の問題をもちている。

このように、ナタン原料の炭酸化反応においては、多かれ少なかれ炭反応ナタン原料のキャリアーオーバーの問題があり、そのために炭酸化条件が制約され、原料の価額及び性状が制限され、更に収率の低下をきたしたりする。

本発明等では、前記ナタン炭化物を含む炭化物のナタン原料を用いてキャリアーオーバーを減少せしめることのできる炭酸化条件を見出すべく、炭化炉内のガス組成の可及的に低い領域で炭化することについて検討を進めた。その結果、ガス組成が空塔炭化速度  $20 \text{ m}^3/\text{分}$  以下と

いつた低い範囲のものであるときはキャリアーオーバーを顯著に抑制することができるものの、炉内炭化物に炭化等の好ましくない現象が発生し、それが帯電体ガス濃度での接触時間の延長とともに増大し、一定時間後には炭化不能になる恐れもあることを確認した。そして帯電ガス濃度の低い領域での炭化に条件が生ずるために炉内炭のガス濃度を高めて炭化物が強い炭化状態になるように炭化含有ガス量を間歇的に変化させることにより、このように好ましくない現象を抑制できること、それによつてガス濃度の低い領域での反応を主体として炭化しキャリアーオーバーを抑制しながら連続的に炭収率で炭化ナタンを製造できることを見出した。

すなわち、本発明は炭酸化炉にナタン原料及び還元性物質を供給し、炭化含有ガスを導入して  $900 \sim 1100^\circ \text{C}$  で炭酸化反応し炭化ナタンを製造する方法において、炉内のガスの空塔炭化速度（反応速度基準）が  $8 \sim 20 \text{ m}^3/\text{分}$  となるように炭化含有ガスを導入し、かつ間歇的に空

塔炭化速度が同炭化速度の  $1.2 \sim 3$  倍の範囲内の値となるように炭化含有ガス導入量を増加させることを特徴とする炭化ナタンの製造方法である。

本発明においては、ナタン原料及び還元性物質を炭化炉内に供給し、炉下部より炭化含有ガスを通常は空塔炭化速度  $5 \sim 20 \text{ m}^3/\text{分}$  の低速度で導入してナタン原料を炭酸化し  $900 \sim 1100^\circ \text{C}$  で炭酸化反応させる。従つてナタン原料としては天然のメタル鉱石の他に各種ナタン炭化物が広く用いることができる。これらは比較的粗粒のものが好ましいが、一歩炭粉を含んでいることを妨げない。還元性物質としては炭粉  $6 \sim 100 \text{ g}$ （タイラー基準、以下同じ）程度の不足、コークス等の固体炭素質還元剤が用いられる。炭酸化反応には炭化含有ガスが用いられるが、このガスは通常と、必要に応じて酸素、空気、その他の不活性ガスを含んだものである。

炭酸化ガスをこのような低速度にすると、炉内原料が加熱したり炭化したりするが、本発明においては間歇的に高速度で炭化含有ガスを

導入してこれらを未然に防ぐことができる。すなわち本発明においては、炉内での炭酸化ガスの空塔炭化速度が間歇的に  $20 \sim 40 \text{ m}^3/\text{分}$  普通は間歇炭化速度の  $1.2 \sim 3$  倍の範囲の速度となるように、炭化含有ガス導入量を変化させる。通常の炭化ガス速度領域と間歇的な高ガス速度領域とのサイクルは、炭酸化炉の大きさ、反応温度、ナタン原料の種類等の相違により異なるが、一般にいえないが、一般に高ガス速度  $0.5 \sim 5$  分と低ガス速度  $3 \sim 30$  分、適ましくは高ガス速度  $1 \text{ 分} \sim 3 \text{ 分}$  と低ガス速度  $8 \text{ 分} \sim 15 \text{ 分}$  とし、適当なサイクルを以てして反復する。炉内のガス速度を間歇的に変えるには油弁かこなされる各種の手段を採用できるが、例えば後記実施例に示されるが如く弁を設けて炭化炉管に絞り弁と電磁弁をもつパイプとを設けて炭化炉管を開閉することによりガス流量を変化させる方法が推奨される。

本発明の炭酸化反応は、主として低いガス速度、すなわち炉内のガスの空塔炭化速度が  $6 \sim 20$

mm/秒で行なわれるので、キャリアーオーバー量反応物を少なくすることができ、また燃焼含有ガスの炉内滞留時間が長くなり、比較的低い温度範囲でも塩素化反応の効率を高めることができる。

図は全配管系例において用いた装置の説明図である。1は炭酸化炉であり、この上端にチタン原料用ホッパー2及び還元性物質用ホッパー3が取り付けられており、チタン原料及び還元性物質はそれぞれスクリューフィーダー4及び5を通じて、炭酸化炉1中に導入される。炭酸化炉1にて生成する反応生成物及び未反応物質はホッパー6を通過してサイクロン7中へ導かれる。サイクロン7では未反応物または炭酸化チタン以外の生成物物質例えば固体の炭化炭等が分離されホッパー8へ導かれる。炭酸化チタンを含むガスはホッパー8を通過して、次の冷却、精製系に送られる。

一方炭酸化炉1下層には導管10を通して塩素、酸素及び窒素が導入される。塩素導入用の

導管15には弁18が、酸素導入用の導管16には弁19が、窒素導入用の導管17には弁20がそれぞれつてあり導管10に接続している。導管10には弁12が付けられており、弁13と電機弁14とが付けられている導管11のバイパスをもっている。

図表1～3は、実施例において用いたチタン原料及び還元性物質の組成性状を示す。なお、右明細書中に於ける重量度は100mmメッシュリターに充填した粉砕体の重量割合を規定し、これを100で割った値である。

表1 チタン原料（炭化法によるチタン酸化物）

TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	重量度	規 格
96.5%	1.4%	1.75%/mm	32-200メッシュのもの 99%以上

表2 チタン原料（天然チタン鉱石）

TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	重量度	規 格
94%	0.6%	2.65%/mm	48-200メッシュのもの 99%以上

表3 還元性物質（石炭コークス）

炭素分	重量度	規 格
95-98%	0.97%/mm	20-80メッシュのもの 99%以上

## 実施例1

図に示すような装置において、内径40mm、高さ180mmの炭酸化炉に表2に記載のチタン原料をホッパー2及びスクリューフィーダー4を通して、また表3に記載の石炭コークスをホッパー3及びスクリューフィーダー5を通してそれぞれ25.0g/時及び6.5g/時の割合で供給した。

一方バルブ12、13、18、19及び20の開口程度を、電機バルブ14を閉じた場合の炭酸化炉内のガスの空塔流速度が15.6mm/秒でしかも導入量が毎分1974/分、酸素304/分となるように、また電機バルブ14を開いた場合の空塔流速度が25.9mm/秒でしかも導入量が毎分3884/分、酸素344/分、窒素894/分となるように設定し、電機バルブ14を8分間閉じて2分間開くよう

作動させて、塩素化ガスを導入し、連続的に塩素化反応をおこなった。この結果、サイクロン7で捕集された未反応チタン原料（キャリアー量）は炭酸化炉1内に導入したチタン原料に対して3.5%にすぎなかった。また炭酸化炉内での炭化は殆どらず、反応温度約1000℃にて連続的に炭酸化チタンを製造することができた。

他方、比較の為に同じ条件で電機弁14を開いたまま運転したところ、キャリアーオーバー量は5.2%であった。また電機弁14を閉じたまま運転したところ、キャリアーオーバー量は少なくなつたが、炭酸化炉1内での部分反応が起つて長時間の運転が不可能であった。

## 実施例2

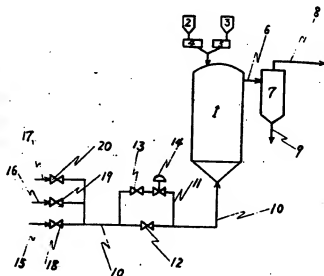
実施例1と同じ装置を用い、表1に記載のチタン原料を20.0g/時、表3に記載の還元性物質を5.5g/時の割合で炭酸化炉1に供給した。また両側にバルブ12、13、18、19及び20の開口程度を予め設定し、電機バルブ14を閉じた場合はガスの空塔流速度が15.6mm/秒でしかも

導入量が毎分170ℓ/分、酸素174ℓ/分、窒素30ℓ/分となるように、また電磁バルブ14を開いた場合は、前記流量が20.8ℓ/秒で、しかも導入量が毎分268ℓ/分、酸素274ℓ/分、窒素47ℓ/分となるようにし、電磁バルブ14を10分間閉じて2分30秒開くよう作動させて、還元化ガスを導入し、連続的に還元化反応をおこなった。この結果、タイタロン7で還元された未反応チタン原料は供給チタン原料に対して僅か2.1多であった。生成した還元チタンは導管6、タイタロン7、導管8を通じて次の冷媒循環系に導かれた。

#### 4. 図面の図号を説明

図は実施例において用いた装置の説明図で、本発明の実施態様の一例を示す。

- |               |               |
|---------------|---------------|
| 1. 還元炉        | 2. チタン原料用ホッパー |
| 3. 還元性物質用ホッパー | 4. スクリューフィーダー |
| 5. タイタロン      | 10. 還元化ガス導入管  |
| 14. 電磁弁       |               |



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## PRODUCTION OF TITANIUM

## Bibliographic data

Description

Claims

INPADOC legal status

Publication number: JP51010803 (B)

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C22B5/02

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GB1355433 (A)

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AU459240 (B2)

AU4507672 (A)

US3825415 (A)

## Cited documents:

JP33009251 (A)

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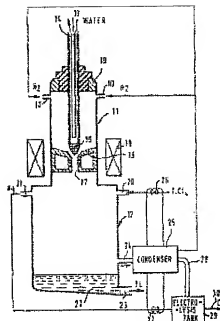
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Abstract not available for JP 51010803 (B)

Abstract of corresponding document: **GB 1355433 (A)**

1355433 Extracting titanium ELECTRICITY COUNCIL 13 July 1972 [28 July 1971] 35535/71 Heading C7D Elemental titanium is obtained by reducing titanium tetrachloride in vapour form with a vapourized alkali or alkaline earth metal, the vapours being heated by hydrogen as carrier gas passed through an electric arc. The reacting materials are maintained at a temperature at which elemental titanium is liquid and falls to the bottom of the reactor vessel 12, and at a temperature at which the temperature of the materials is above that of the boiling point of the alkali or alkaline earth metal chloride formed so that the chloride thus formed may be removed from the reaction vessel 12 through 24. The metal contained in this chloride is obtained by electrolysis in tank 29 and passed into the reactor vessel 12 through ports 21. The titanium tetrachloride is passed through port 20 and the arc is struck between the cathode tip 15 and anode 16, a swirling action of the gas passed down through nozzle 17 being caused by the effect of an electrically energized coil 18 on the arc struck.



④ Int. Cl.<sup>2</sup>  
C 22 B 34/12  
C 22 B 5/02

⑤ 日本分類  
10 E 121  
10 A 21

⑥ 日本国特許庁

⑦ 特許出願公告

昭51-10803

# 特 許 公 報

⑧ 公告 昭和51年(1976)4月7日

庁内整理番号 7047-42

発明の数 2

(全4頁)

1

## ⑨ チタンの製造法および装置

① 特 願 昭 47-74706

② 出 願 昭 47(1972)7月27日

公 開 昭 48-23610

③ 昭 48(1973)3月27日

優先権主張 ④ 1971年7月28日 ⑤ イギリス国 ③ 5535/71

⑥ 発 明 者 ファリップ・ダグラス・ジョンストン

イギリス国 チェスター・ラムレイ・ロード3

同 ジェームス・ロートン

イギリス国 チェスター・ロークリフ・アベニュー49

同 アイアン・マツキイソン・パーカー  
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## ⑨ 特許請求の範囲

1 蒸気状四塩化チタンと蒸気状アルカリ金属またはアルカリ土類金属とを反応させて四塩化チタンから元素状チタンを製造する方法において、上記反応剤の蒸気をアーク中を通過する担体ガスを形成する水素によつて加熱して、生成する元素状チタンが液状にあり且つ使用するアルカリ金属またはアルカリ土類金属と四塩化チタン中の塩素との結合により生成する塩化物の沸点より高い温度に上記反応剤を保持し、生成した該塩化物および他の希望せざる生成物を蒸気状にて除去することを特徴とする四塩化チタンから元素状チタンの製

造法。

2 反応室と、アルカリ金属およびアルカリ土類金属よりなる群から選択される蒸気状金属を該反応室に注入する装置と、蒸気状四塩化チタンを該

5 反応室に注入する装置と生成した元素状チタンを該反応室から取り出す装置よりなる四塩化チタンから元素状チタンを製造する装置において、該反応室の頂部にアーク用電極と該電極によつて形成されてるノズルと電極間のアークによつて加熱されノズルを通して担体ガスとして水素を注入する装置が備えられており、蒸気状四塩化チタンおよび蒸気状アルカリ金属または蒸気状アルカリ土類金属をノズルから流出する高温水素流と交差する方向で反応器に注入し、且つ反応室から生成した

15 アルカリ金属の塩化物蒸気またはアルカリ土類金属の塩化物蒸気を取り出す装置を備えたことを特徴とする四塩化チタンから元素状チタンを製造する装置。

## 発明の詳細な説明

本発明は四塩化チタンを還元することにより元素状チタンを製造する方法および装置に関する。

現在チタンを工業的に大規模に製造するために使用されてる方法では、不純な酸化チタンを塩素化して四塩化チタンを製造し、生成した四塩化チタンを精製した後で例えばマグネシウムまたはナトリウムを用いて不活性ふん囲気内で還元する。この方法で得られるチタンはスポンジ状で、過剰量の還元剤および還元剤金属の塩化物例えば塩化ナトリウムまたは塩化マグネシウムにより汚染されている。従つて、機械加工に使用できる形態の金属チタンを得るには、スポンジチタンを費用のかかる長時間の精製処理をしなければならない。この結果、チタンの製造原価が高くなり、かかる高価格のために金属チタンの使用範囲は現在制限されている。

本発明の目的は四塩化チタンから直接使用できる形態の金属チタンを製造する秀れた方法および

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装置を提供することにある。

本発明は、蒸気状四塩化チタンと蒸気状アルカリ金属またはアルカリ土類金属とを反応させて四塩化チタンから元素状チタンを製造するにあたり、上記反応剤の蒸気をアークを通過する担体ガスを形成する水素によって加熱して、生成する元素状チタンが液状にあり且つ使用するアルカリ金属またはアルカリ土類金属還元剤金属と四塩化チタン中の塩素との結合により生成する塩化物の沸点より高い温度に上記反応剤を保持し、生成した該塩化物および他の希望せざる生成物を蒸気状にて除去することを特徴とする四塩化チタンから元素状チタンを製造する方法に関する。

アルカリ金属またはアルカリ土類金属としてはナトリウムまたはマグネシウムを使用するのが好ましい。他のアルカリ金属またはアルカリ土類金属例えばカリウム、カルシウム、ストロンチウムまたはバリウムも使用してよいが、然しナトリウムよりも高価である。かかる物質を使用する場合には、反応はチタンの融点よりも高い温度例えば1800ないし2500℃の温度範囲で実施できる。

本発明法は反応を気相で実施する。然も本発明法の反応温度では元素状チタンは液体であるので反応容器の底に落下する。そして不純物は蒸気状にあり、且つ反応容器の底にある熔融金属チタンの表面よりも充分高い位置で反応が行われるので、不純物が冷却して熔融金属中に混入することができない。従って高純度の金属チタンを得ることができる。

生成したチタンは液状で取り出してもよいし、または一部分または完全に固化させてもよい。後者の場合にはチタンを定期的に取り出す。不純物および他の反応生成物は蒸気として取り出す。

アルカリ金属またはアルカリ土類金属は反応容器内に蒸気として注入してもよいし、または液体として注入してもよい。液体として注入した場合には、液体の金属は反応容器内の高温により蒸発するので、反応は気相で行われる。同様に、四塩化チタンは蒸気としてまたは液体として注入でき、後者の場合には反応容器内で蒸発する。

担体ガスはアーク放電からの熱をアルカリ金属またはアルカリ土類金属蒸気および四塩化チタン蒸気に伝達するのに適したガスを使用することを

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要する。アルカリ金属またはアルカリ土類金属蒸気または四塩化チタン蒸気をアーク（電弧）中を通過することによつてこれらの蒸気を直接加熱することができるが、この場合には安定性の問題がある。この理由により担体ガスを使用するのが有利である。担体ガスとしては、チタンと有害な反応を行わず、且つ放電特性が秀れた場合即ち安定なアーク放電を生ずると共に電圧および電流特性に関して好適に合致する場合にはいかなる担体ガスを10使用してもよい。有効に伝熱するためには、単位容積当りエンタルピーの大きい気体が好ましい。水素はかかる必要条件を満たすのに最も適したガスである。水素は還元性ガスであり、また安定放電を生ずる秀れた放電特性を有するので有利である。アルゴンのような不活性ガスも使用でき、必要量の熱量を伝達するには水素の3倍もの多量のアルゴンを使用する必要がある。更に、反応容器には反応剤の分圧を低下させる unnecessary ガスを多量に供給してはならない。この理由により、担体ガスとして水素を使用するのが好ましい。

反応生成物として得られる塩化物、即ちアルカリ金属の塩化物またはアルカリ土類金属の塩化物は別の処理工程で電解して反応容器に蒸気状で供給するためのアルカリ金属またはアルカリ土類金属を得ることができる。四塩化チタンおよびアルカリ金属またはアルカリ土類金属は反応容器に注入する前に、熱交換器を用いて反応容器から出てくる塩化物蒸気および（または）液体チタンから得られる熱によつて予熱または蒸発させる。

更に本発明は、反応室と、アルカリ金属およびアルカリ土類金属よりなる群から選択される蒸気状金属を該反応室に注入する装置と、蒸気状四塩化チタンを該反応室に注入する装置と、生成した元素状チタンを該反応室から取り出す装置よりなる四塩化チタンから元素状チタンを製造する装置において、該反応室の頂部にアーク用電極と該電極によつて形成されてるノズルと電極間のアークによつて加熱されノズルを通して担体ガスとして水素を注入する装置が備えられており、蒸気状四塩化チタンおよび蒸気状アルカリ金属または蒸気状アルカリ土類金属をノズルから流出する高温水素流と交差する方向で反応容器に注入し、且つ反応室から生成したアルカリ金属の塩化物蒸気またはアルカリ土類金属の塩化物蒸気を取り出す装置



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を備えたことを特徴とする四塩化チタンから元素状チタンを製造する装置に関する。

本発明の装置には上記電極を收容するアーク室を設け、上記電極を同心状にしそして反応容器に通ずるノズルを形成する形状にし、上記アーク室に好ましくは切線方向に担体ガス注入口を備えるのが好ましい。

次に本発明を添付図面を参照して蒸気化四塩化チタンから金属チタンを製造する1例につき説明する。

添付図面において、管10を経て反応容器12内のアークヒーターに対する円筒形区域11の切線方向の導入口に水素ガスを供給する。アークヒーターにはタングステンチップ15を支持する同心管13および14から形成された水冷カソードを設け、水は内管13を通過して流入しそして外管14から戻す。タングステンチップ15と、タングステンチップ15と協働してノズル17を形成する形状にした円筒形水冷銅アノード16との間にアーク（電弧）を生ぜしめ、円筒形区域11からノズル17を通過して反応室内にガスを下方に流す。電気的に付勢したコイル18により軸線方向の磁界が生成し、これによりアーク（電弧）が回転してノズルから出るガス流中に渦流および乱流を生ぜしめる。アノードとカソードとの間の絶縁を絶縁ブロック19により形成し、絶縁ブロック19にカソード構成体を貫通させる。主反応剤と混合した後に混合物の温度が約1800ないし2500℃になるような温度に水素ガスを加熱するようにアークヒーターを配置する。液状または蒸気にした四塩化チタンを反応容器内に20から注入し、液状または蒸気にしたナトリウムを反応容器内に21から注入する。上記反応剤を液状に注入する場合には、これらの反応剤は反応容器内で蒸発する。ノズル17から高圧の水素ガス流は四塩化チタン蒸気および還元剤金属蒸気と交差して相互に作用して上記諸物質の温度を上昇し、四塩化チタンはナトリウムにより次の反応式によつて還元される。



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この反応は気相で起る。四塩化チタンおよびナトリウムは反応室の頂部付近の隔壁を経て注入する。金属チタンは22で凝縮し捕集され23から取り出される。塩化ナトリウム蒸気、水素およびチタンの下級塩化物は24から抜き取り、塩化ナトリウムを熱交換器25で凝縮する。この熱交換器25からの熱を添付図面に示す如く26と27で利用して反応容器に注入する四塩化チタンおよび金属ナトリウムを予熱し、蒸気にする。凝縮した塩化ナトリウムを管28により電解タンク29に導入し、ここで上記塩化ナトリウムを電解してナトリウムを製造し、生成したナトリウムを管21から反応容器内に供給する。電解タンク29からの塩素は30で除去する。凝縮器（熱交換器25）から流出する水素および他の残存ガス状生成物を管10により担体ガスとして反応容器中に再循環する。

銅アノードを使用する代りに水冷チタンアノードを用いて反応容器内に生成する金属チタン中に不純物が混入する危険を最小にすることができる。同様に、タングステンチップ15の代りにチタンチップをカソード用に使用することができる。

次に本発明の実施の態様を示す。

- (1) 反応を1800ないし2500℃の範囲内の温度で実施する特許請求の範囲第1項記載の方法。

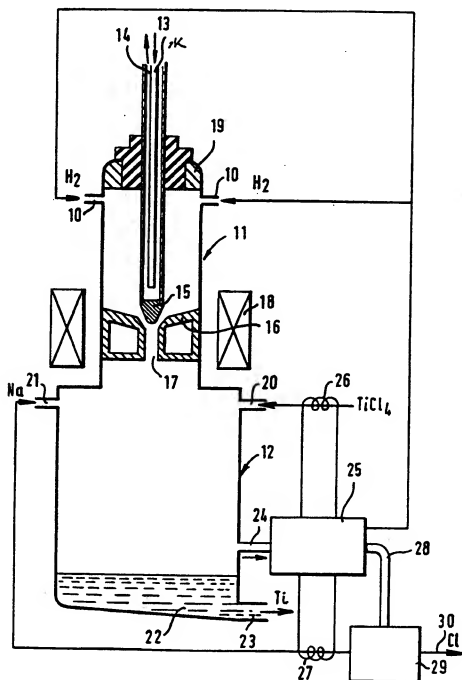
#### 図面の簡単な説明

添付図面は四塩化チタン蒸気から金属チタンを製造するための反応容器および付属装置を図解的に示す図面である。

11……円筒形区域、12……反応容器、13……内管、14……外管、15……タングステンチップ、16……銅アノード、17……ノズル、18……コイル、19……絶縁ブロック、25……熱交換器、29……電解タンク。

◎引用文献

特 公 昭 33-9251



# EUROPEAN PATENT OFFICE

## Patent Abstracts of Japan

PUBLICATION NUMBER : 60255300  
PUBLICATION DATE : 16-12-85

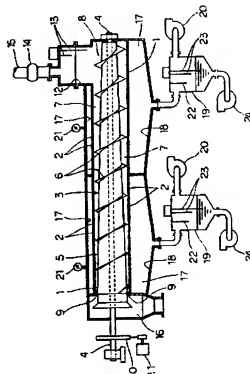
APPLICATION DATE : 31-05-84  
APPLICATION NUMBER : 59112064

APPLICANT : YAMATO SANGYO KK;

INVENTOR : AOYAMA YOSHIRO;

INT.CL. : B30B 9/14 C02F 11/12

TITLE : SCREW PRESS TYPE SLUDGE  
DEHYDRATOR



**ABSTRACT :** PURPOSE: To dehydrate sludge with high dehydrating power by disposing a filter cylinder for compressive dehydration of the sludge into evacuation chambers and evacuating the inside of said chambers to desired pressures according to the characteristics of the sludge to be dehydrated.

**CONSTITUTION:** The half on the high-pressure side of the filter cylinder 1 and the half on the low-pressure side thereof are disposed into the respectively segmented evacuation chambers 17. The chambers 17 are made evacuable by the respectively regulated suction forces to be generated by vacuum pumps 20. The pumps 20 in such constitution are driven to evacuate the inside of the chambers 17 to the desired pressures and a variable speed motor 11 is driven to rotate a screw shaft 3 at a desired speed. The sludge charged through a sludge feed port 12 is passed through a compressing passage 7 and while the sludge is gradually compressed by the screw shaft 3, the sludge is moved toward an outlet 9, by which the sludge is dehydrated; at the same time the sludge is dehydrated by the evacuation. The dehydrated sludge is dropped through the outlet 9 into a sludge dropping path 16.

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# PATENT ABSTRACTS OF JAPAN

(11)Publication number : **61-012837**  
 (43)Date of publication of application : **21.01.1986**

(51)Int.Cl. **C22B 34/12**

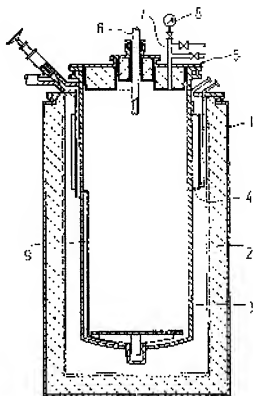
(21)Application number :	<b>59-133576</b>	(71)Applicant :	<b>ISHIZUKA HIROSHI</b>
(22)Date of filing :	<b>28.06.1984</b>	(72)Inventor :	<b>ISHIZUKA HIROSHI</b>

## (54) MANUFACTURE OF METALLIC TITANIUM

### (57)Abstract:

**PURPOSE:** To control the contamination of formed metallic Ti by the elements of the vessel material by introducing an inert gas into the space over the bath surface in a vessel to pressurize the space to specified pressure when  $TiCl_4$  is supplied onto the bath surface of molten Mg in a cylindrical steel vessel through a piping means.

**CONSTITUTION:** A cylindrical steel vessel 3 is furnished in an electric heating furnace 1, metallic Mg is packed into the vessel 3, an inert gas is supplied into the space of the furnace and the vessel 3, and the Mg is heated and melted by a heater 2. Then  $TiCl_4$  is blown from a supply pipe 6 onto the part around the center of the bath surface of molten Mg, and allowed to react with the Mg to deposit metallic Ti and  $MgCl_2$ . Sponge metallic Ti is recovered in this way. At this time, the pressure of the inert gas in the space over the bath surface in the vessel 3 is kept at  $\geq$  about 0.5kg/cm<sup>2</sup> gauge pressure to carry out the reaction. Consequently, the reaction proceeds mainly at the part of the bath surface distance from the wall surface, and the contamination of deposited metallic Ti by the elements of the vessel wall material is controlled.



## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 64-047823

(43)Date of publication of application : 22.02.1989

(51)Int.Cl.

C22B 34/12

(21)Application number : 62-203159

(71)Applicant : TOHO TITANIUM CO LTD

(22)Date of filing : 17.08.1987

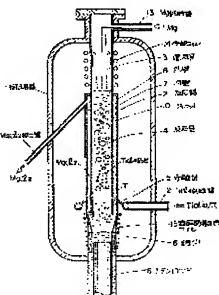
(72)Inventor : OKUDAIRA SHIGENORI  
 IRIE TAKEFUMI  
 UCHIDA HIROSHI  
 FUKAZAWA HIDEKAZU  
 KOBAYASHI KAZUHIKO  
 YAMAGUCHI MASANORI

## (54) PRODUCTION OF METALLIC TITANIUM

## (57)Abstract:

PURPOSE: To improve the velocity and efficiency of the reaction at the time of reducing titanium tetrachloride with a reducing metal by setting the temp. in a reactor at the melting point or above of the reducer, etc., and the pressure in the reactor at the vapor pressure or above of reducing metallic chloride.

CONSTITUTION: The temp. in the reactor 2 charged with reducing metallic chloride is retained at the melting point or above of the reducers metal and metallic chloride. The pressure in the reactor 2 is furthermore retained at the vapor pressure or above corresponding to the above-mentioned temp. of said chloride. Gaseous titanium tetrachloride is poured into the reactor from a feed tube 12 equipped on the lower side of a molten bath of said chloride. The reducing metal is then fed from a feed tube 13 equipped on the upper side of said molten bath to bring titanium tetrachloride into reaction with the reducing metal. Generated metallic titanium is then continuously extracted.



**TRANSLATION OF NORWEGIAN PATENT  
NO. 90840**

*Cl. 40a<sup>46.50</sup> – Int. Cl. C 22 b –*

<b>Publication Date</b>	:	27 January 1958
<b>Date of Grant</b>	:	30 November 1957
<b>Filing Date</b>	:	3 June 1955
<b>Proprietor</b>	:	The Central Institute for Industrial Research, Blindern, Oslo
<b>Inventor</b>	:	Finn J. Langmyhr, Cand.real.
<b>Attorney</b>	:	Dr. Ing. Harald Aarflot of Bryn & Aarflot, Oslo
<b>Title</b>	:	"A Process for the Manufacture of Titanium."

## **A Process for the Manufacture of Titanium**

The present invention pertains to a process for the manufacture of titanium by reduction of titanium tetrachloride with molten alkali or earth alkali metals, or a mixture of these metals.

Titanium has until now essentially been manufactured according to the so-called Kroll process consisting of letting titanium tetrachloride drip down into the molten magnesium. This process with appurtenant apparatus is originally described in US Patent no. 2,205,854. A series of patents has later been granted for various modifications of the original Kroll process. Examples of such patents are:

US Patents nos. 2,564,337; 2,567,837; 2,607,674; 2,621,121; 2,647,826 and British Patent no. 638,840.

More recently the reduction of titanium tetrachloride with sodium has also gained increasing use, and a number of patents has been granted for various processes and apparatus which use sodium as reducing agent. An example of a patent of this type is British Patent no. 717,930, corresponding to Norwegian Patent no. 84,847.

However, for the time being neither the Kroll process nor methods using sodium as reduction agent can produce titanium at prices which allow a general use of the metal as a constructional material, and it is therefore of great importance that experiments for developing improved production processes be carried out.

The present invention relates to a process for the reduction of titanium tetrachloride by means of molten alkali or earth alkali metals, or a mixture of these metals.

The improvements achieved by the present invention are, when compared with known methods and apparatus for the manufacture of titanium by thermal reduction of titanium tetrachloride, for the first that the reaction products by means of the centrifugal force are continuously removed from the reaction zone, whereby the hazard to formation of lower titanium chlorides is eliminated or possibly diminished, and for the second that the process makes the continuous manufacture of titanium possible.

In US Patent no. 2,395,286 it was previously suggested to use a centrifuge in connection with a process for the manufacture of titanium by aluminothermal

reduction of titanium dioxide. According to this patent, the titanium resulting from the reduction and which is in a liquid state, is to be separated from the other reaction products by centrifugation. However, as titanium in molten state attacks all known ceramic materials, it is scarcely likely that the process suggested in the said US Patent could deliver a sufficiently pure titanium. In all processes which aim at the manufacture of ductile titanium and where thermal reduction is used, it must be considered to be very important that the reduction is effected at so low a temperature that the titanium does not attack the materials in the reactor.

In the process according to the invention, titanium is manufactured by reduction of titanium tetrachloride with a molten alkali or earth alkali metal, including magnesium, or a mixture of these metals, and the process is carried out in the way that titanium tetrachloride is introduced into the molten reduction agent which is located in a centrifuge rotating with a speed so that the titanium resulting from the reduction and the formed alkali or earth alkali metal chloride are separated from the molten reduction agent thereby that the reaction products by the centrifugal force are pressed against the wall of the centrifuge, whereupon they are removed therefrom.

The centrifuge being used is, according to a first embodiment, cylindrical and provided with a scraper device for the removal of the reaction products. The centrifuge can also according to a further embodiment be given a conical shape so that the reaction products are continuously removed thereby that they glide upwards along the wall of the centrifuge and are then flung out therefrom.

The centrifuge is further suitably heated by means of electrical heating elements enclosed in the wall of the centrifuge. The titanium is continuously or discontinuously charged below or over the surface of the reduction agent in the centrifuge. The reduction agent is also continuously or discontinuously in solid or molten state charged into the centrifuge.

The centrifuge with appurtenant supply lines and optional scraper device is built into a room wherein an inactive atmosphere, e.g. argon, can be maintained. The supply lines and the scraper device as well as thermocouples for the reading of the temperature and electrical conduits for the heating of the centrifuge are gas-tightly passed through the walls of the room in which the centrifuge is situated. The same applies of course to the shaft of the centrifuge as the drive means for the centrifuge is arranged outside the gas-tight room.



In Figures 1a and 2 there are, in section, schematically shown two embodiments of apparatus for the carrying out of the process.

A centrifuge *a* with a cylindrical design (Fig. 1a) or conical design (Fig. 2) and which rotates with variable speed on the vertical hollow shaft *f*, contains the reduction agent *b*. The centrifuge is constructed of heat resistant steel covered on its interior with a layer of the same material or a layer of molybdenum, tungsten or tantalum or of a ceramic material, e.g. aluminium oxide. The exterior of the centrifuge is provided with electrical resistance heating. The resistance wire is covered by a layer of insulation mass. The insulation mass is kept in place by an outer mantle. The supply of electrical energy for the heating is effected through the hollow shaft provided with sliding contacts (these are not shown in Fig. 1a or Fig. 2). Through the tube *c*, which is arranged axially in relation to the centrifuge and which can be moved vertically, the supply of titanium chloride vapour or a mixture of titanium tetrachloride vapour and argon is effected. The lower end of the tube *c* has radially arranged outlet openings. A thermocouple *g* which indicates the temperature in the metal during the reduction is attached to the tube *c*. The supply of reduction agent is effected through the tube *d*. The material of the supply tubes *c* and *d* is heat resistant steel. For the removal of the reaction products, the cylindrically designed centrifuge (Fig. 1a) is provided with a movable scraper *e*. In Fig. 1b, the scraper *e* is drawn seen from the side and from above. The scraper is constructed of heat resistant, perforated steel plate and is designed so that it can glide tightly along the bottom and walls of the centrifuge and collect the reaction products simultaneously with the straining off of the major amount of entrained reduction agent. The whole centrifuge is built in into a gas-tight room constructed of heat resistant steel. This room is provided with passages for the shaft *f*, the supply tube *c* and *d*, the scraper *e*, thermocouple *g* and an outlet tube for argon. The shaft *f*, tube *c* and scraper *e* are movable in gas-tight, cooled bearings. On the bottom of the gas-tight room is a larger opening which permits the emptying of the reaction products.

The process according to the invention will be particularly well suited for a reduction of titanium tetrachloride with sodium. Because of this, a more explicit report will be given below regarding in what way this reduction can be carried out in the apparatus described in the foregoing.

The following physical data is of importance to the reduction:

	Density	Melting point °C	Boiling point °C
Na	0.97	97.5	880
NaCl	2.165	801	c. 1450
Ti	4.5	1660	-
TiCl <sub>4</sub>	1.73	-30	136

The process for reducing titanium tetrachloride with sodium will then briefly be as follows:

The gas-tight room containing the centrifuge is filled with argon by means of the supply tube *c*. During the further reduction process a little excess of argon is maintained. The centrifuge is then heated to a temperature somewhat below the temperature at which the reduction is to be effected. Through the tube *d* molten sodium is added, the tube *c* with the thermocouple *g* is lowered into the molten metal and the centrifuge is heated to the temperature at which the reduction is to be carried out. The reduction with sodium is effected at a suitable temperature in the temperature range 100-700°C. The centrifuge is then set into rotation and the mixture of argon and titanium tetrachloride is pressed into the melt through the outlet wholes in the tube *c*. Reduction to metallic titanium takes place momentarily and the reaction products titanium and sodium chloride are by the centrifugal force pressed upwards against the wall of the centrifuge, while novel amounts of titanium tetrachloride and sodium are charged.

The further process will be dependent on which of the two types of centrifuge that is utilised. In a centrifuge with cylindrical design, the supply of titanium tetrachloride and sodium time must be stopped after a certain, the speed of the centrifuge is decreased and the scraper *e* is lowered along the wall of the centrifuge. Under slow rotation the reaction products are scraped off from the wall and bottom of the centrifuge and are emptied of the rim down into the bottom of the surrounding gas-tight room. The reduction process can then be started again.

In a centrifuge of conical design, the reduction proceeds continuously, as the reaction products contaminated with entrained sodium slides upwards along the wall of the centrifuge and are then flung off.

Th titanium manufactured, mixed with sodium chloride and entrained sodium, is coll cted at the bottom of the gas-tight room. In this gas-tight room or in another gas-tight room filled with argon, the excess of sodium is removed thereby

that the mixture is centrifuged at a suitable temperature, e.g. 150°C, in a centrifuge with cylindrical perforated walls. The sodium removed in this way can be re-used for reduction of titanium chloride. The titanium mixed with sodium chloride and possible remnants of sodium are removed from the centrifuge, purified by leaching with water and diluted acid and is at last melted down in a voltaic arc furnace.

**Pat nt Claim**

1. A process for the manufacture of titanium by thermal reduction of titanium tetrachloride by means of molten alkali or earth alkali metals, or a mixture of these metals, characterised in that the reaction is carried out in a centrifuge rotating with such speed that the titanium resulting from the reaction and the formed alkali or earth alkali metal chloride are separated from the molten reduction agent thereby that the reaction products by means of the centrifugal force are pressed against the wall of the centrifuge, whereupon they are removed therefrom.
2. A process according to claim 1, characterised in that the centrifuge is cylindrical and that it for removal of the reaction products is provided with a scraper device.
3. A process according to claim 1, characterised in that the centrifuge has a conical design so that the reaction products are continuously removed thereby that they glide upwards along the wall of the centrifuge and out from the centrifuge.
4. A process according to claims 1 to 3, characterised in that the centrifuge is heated.
5. A process according to claims 1 to 4, characterised in that the centrifuge is built in into a room where an inactive atmosphere is maintained.

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Cited publications: None

One page of drawings (2 figures)

FIG. 1.

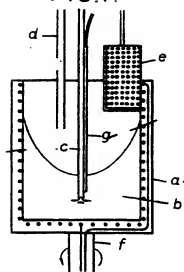
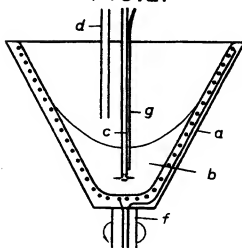


FIG. 2.



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Государственный комитет  
Система Министров СССР  
по делам изобретений  
и открытий

# О П И С А Н И Е ИЗОБРЕТЕНИЯ

К АВТОРСКОМУ СВИДЕТЕЛЬСТВУ

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## СПОСОБ МЕТАЛЛОТЕРМИЧЕСКОГО ПОЛУЧЕНИЯ ПОРОШКОВ ТУГОПЛАВКИХ МЕТАЛЛОВ

Изобретение относится к производству порошков тугоплавких металлов металлтермическим восстановлением.

Известен способ металлтермического получения порошков тугоплавких металлов, заключающийся в том, что восстановление хлорида, например титана, осуществляют металл-восстановителем, например магнием, причем процесс ведут при непрерывной циркуляции жидкости восстановителя и образующегося хлорида, полученную суспензию порошка в металл-восстановителе удаляют из реактора.

Предлагаемый способ отличается от известного тем, что, с целью повышения однородности порошка и предотвращения осаждения частиц на стенках реактора, осуществляют направленную циркуляцию металла-восстановителя, который в виде струи подают в реакционную зону навстречу парам хлорида, и процесс восстановления проводят на поверхности образующихся и находящихся во взвешенном состоянии частиц-зародышей тугоплавкого металла до тех пор, пока укрупненные частицы под действием гравитационных сил не уходят в отстойник, откуда их удаляют из под слоя жидкого хлорида металла-восстановителя.

На чертеже изображена схема установки,

на которой может быть осуществлен предлагаемый способ.

Способ осуществляется следующим образом.

Жидкий металл-восстановитель, например магний, подают из котла-отстойника 1 в реакционную камеру 2 с помощью центробежного насоса 3, причем металл подают в реакционную камеру 2 в виде непрерывно циркулирующей вертикальной струи. Навстречу струе поступают пары хлорида тугоплавкого металла, например четыреххлористого титана.

В реакционной зоне происходит образование частиц-зародышей тугоплавкого металла и дальнейший процесс восстановления паробразного хлорида протекает главным образом на поверхности твердой фазы. Рост зародышей порошка происходит преимущественно во время прохождения их через реакционную камеру 2.

Образовавшиеся частицы в струе жидкого металла находятся во взвешенном состоянии и непрерывно циркулируют в ней до тех пор, пока не достигнут определенного размера. По мере укрупнения они осаждаются под действием гравитационных сил в нижнюю часть котла-отстойника 1. Размер частиц порошка определяется соотношением скорости их осаждения к скорости циркуляции металла-вос-

становителя, и поэтому может регулироваться изменением кратности циркуляции.

Таким образом, предлагаемая технология обеспечивает получение порошков однородного гранулометрического состава, не содержащего пирофорных фракций.

Осадивший порошок тугоплавкого металла, например титана, скапливается в нижней части котла-отстойника 1 под слоем жидкого хлористого металла-восстановителя, например магния, откуда он выгружается с помощью шнека 4.

Пример. 2—2,5 кг жидкого магния подают в предварительно заполненный аргоном и нагретый до температуры 700°C котел-отстойник 1, затем включают центробежный насос 3 и регулируют число оборотов таким образом, чтобы фонтанируемый жидкий магний не достигал крышки реакционной камеры 2. Далее тетрахлорид титана подают с такой скоростью, чтобы реакция восстановления в основном проходила в средней части реакционной камеры 2. О положении реакционной зоны можно судить по показаниям термопар, расположенных на различной высоте реакционной камеры 2.

В зоне прохождения реакции развивается наиболее высокая температура.

По мере накопления титанового порошка под слоем хлористого магния его выгружают шнеком 4 в приемник, а в котел-отстойник 1 подают новую порцию магния.

В таблице приведен гранулометрический состав различных образцов титанового по-

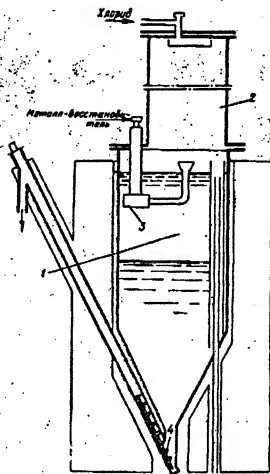
рошка, полученного по предлагаемой технологии.

№ пробы	Содержание фракции, %			
	+ 6,4 мкм	- 0,4 + + 6,1 мкм	- 0,1 + + 0,15 мкм	- 0,15 мкм
1	16,0	72,2	11,0	0,2
2	16,5	74,6	7,6	1,3
3	16,5	68,1	13,4	2,0
4	18,9	73,3	6,5	1,3
5	21,3	70,7	5,1	2,9

### Предмет изобретения

Способ металлотермического получения порошков тугоплавких металлов восстановлением их хлоридов циркулирующим жидким металлом-восстановителем, отличающийся тем, что, с целью повышения однородности порошка и предотвращения осаждения частиц на стенках реактора, циркуляции подвергают металл-восстановитель, который в виде струи подают в реакционную зону навстречу парам хлорида; и процесс восстановления проводят во взвешенном состоянии частиц-зародышей тугоплавкого металла до тех пор, пока укрупнительные частицы под действием гравитационных сил не уходят в отстойник, откуда их удаляют из-под слоя жидкого хлорида металла-восстановителя.

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# TRANSLATION

RUSSIAN PATENT 411962

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Inventor: V. H. Yevdokimov

Applicant: Institute for new chemical problems AN SSSR

## METHOD FOR METALLOTHERMAL OBTAINING OF POWDERS OF DIFFICULTLY FUSIBLE METALS

The invention relates to the production of powders of difficultly fusible metals by metallothermal reduction.

There is known a method of metallothermal obtaining of powders of difficultly fusible metals, consisting in that the reduction of the chloride, for example of titanium, is performed by a metal-reducing agent, for example magnesium, in which the process is conducted with continuous percolation of the liquid of a reducing agent forming the chloride; the suspension obtained of the powder in the metal reducing agent is removed from the reactor.

The proposed method is distinguished from the known method in that, with the aim of improving the homogeneity of the power and of preventing the settling of particles on the walls of the reactor, there is brought about an aiming of the circulation of the metal-reducing agent, which in the form of a jet falls into

the reaction zone toward the chloride vapors, and the process of reduction is conducted on the surface of the seed particles of the difficultly fusible metal, forming and present in a suspended state, until the enlarged particles under the action of gravitational forces go into a settling tank, from where they are removed from under the layer of liquid chloride of the metal-reducing agent.

In the drawing there is represented the schema (diagram) of the apparatus on which it is possible to execute the proposed method.

This method is realized in the following manner:

A liquid metal-reducing agent, for example magnesium, is fed from the settling tank 1 into the reaction chamber 2 with the aid of a centrifugal pump 3, in which process the metal is sent into the reaction chamber 2 in the form of a continuously circulating vertical jet. To meet the jet there enter chloride vapors of the difficultly fusible metal, for example titanium tetrachloride.

The particles forming in the jet of liquid (molten) metal are present in a suspended state and circulate continuously in it until they achieved a determined dimension. As they are enlarged they settle under the action of gravitational forces in the lower part of the settling tank 1. The size of the powder particles is

determined by the relation of the speed of their settling to the speed of circulation of the metal-reducing agent, and for this reason can be regulated by alternation of the amount of circulation.

Accordingly, the proposed technology provides for the obtaining of powders of homogeneous granulometric composition, not containing pyrophoric fractions.

The settling powder of the difficultly fusible metal, for example, titanium, accumulates in the lower part of the settling tank 1 under a layer of liquid chloride metal-reducing agent, for example magnesium, from where it is discharged with the aid of the worm 4.

Example. 2-2.5 kg. of liquid magnesium are placed in a settling tank preliminarily filled with argon and heated to a temperature of 700°C. There is then engaged the centrifugal pump 3 and the number of revolutions is regulated in such manner that the spouting liquid magnesium does not reach the roof of the reaction chamber 2. Furthermore, titanium tetrachloride falls with such speed that the reduction reaction proceeds essentially in the middle part of the reaction chamber 2. It is possible to judge the position of the reaction zone by the indication of thermocouples disposed at different height(s) of the reaction chamber 2.

The highest temperature is developed in the zone of passage of the reaction.

As the titanium chloride accumulates under the layer of magnesium chloride, it is discharged by the worm 4 into a receiver, and a new portion of magnesium is placed in the settling tank 1.

In the table there is presented the granulometric composition of different samples of titanium powder obtained by the proposed technology.

Fraction No.	Content of fraction, %			
	+ 0.4mm	-04. + + 0,1 mm	- 0.1 + + 1.15 mm	- 0.15(?) mm
<u>Cf. Original figures are somewhat illegible</u>				
1	16.6	72.2	11.0	0.2
2	16.5	74.6	7.6	1.3
3	16.5	68.1	13.4	2.0
4	18.9	73.3	6.5	1.3
5	21.3	70.7	5.1	2.9

Object of Invention (Claim)

Method for metallothermal obtaining of powders of difficultly fusible metals by reduction of their chlorides by a circulating liquid reducing agent, characterized in that, with the aim of improving the homogeneity of the powder and preventing the settling of particles on the walls of the reactor, there is circulated a metal-reducing agent which, in the form of a jet, is sent into the reaction zone toward the chloride vapors, and the reduction process is conducted on surfaces that have formed and are present in a suspended state of the embryonic particles of the difficultly fusible metal until the enlarged particles under the action of gravitational forces pass into a settling tank, from which they are removed under a layer of liquid chloride of the metal-reducing agent.